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**PHYSIO-CHEMICAL EVALUATION AND FUNCTIONAL ASSESSMENT  
OF NATIVE WETLAND SOILS AND ORGANIC AMENDMENTS  
FOR FRESHWATER MITIGATION WETLANDS**

A Thesis Presented

By

Emily K.D. Stockman

Submitted to the Graduate School of the  
University of Massachusetts Amherst in partial fulfillment  
of the requirements for the degree of

MASTER OF SCIENCE

May 2007

Plant, Soil and Insect Sciences

Division of Plant and Soil Sciences



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Approved as to style and content by:

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Peter Veneman, Chair

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Deborah Picking, Member

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Baoshan Xing, Member

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Peter Veneman, Department Head  
Department of Plant, Soil & Insect Sciences

## DEDICATION

This thesis is dedicated to my husband, Ty, the most important decision I've ever made. Everything else is icing on the cake.

## ACKNOWLEDGMENTS

Foremost, I would like to thank Dr. Deborah Picking for believing in me, had it not been for her I would not have taken this particular journey at this particular time.

I would like to express my gratitude to Dr. Peter Veneman and Dr. Baoshan Xing for their thoughtful suggestions and assistance in editing this manuscript.

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I would like to thank my friends and family for their tremendous love and support. I'm done now and looking forward to returning many favors.

A "ginormous" thanks to Dr. Mickey Spokas (Dirt Mama) and Dr. Elizabeth Johnson (Dirt Lady). It has been said that one is fortunate to go through life with one good friend. I am truly a blessed woman, for I have two.

To my son, Henry, who continues to take my breath away, thank you for keeping everything in perspective.

Finally, I would like to thank my husband, Ty. We did it! I love you, with all my heart, always.

## **ABSTRACT**

### **PHYSIO-CHEMICAL EVALUATION AND FUNCTIONAL ASSESSMENT OF NATIVE WETLAND SOILS AND ORGANIC AMENDMENTS FOR FRESHWATER MITIGATION WETLANDS**

MAY 2007

EMILY K.D. STOCKMAN, B.S., UNIVERSITY OF MASSACHUSETTS AMHERST

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Directed by: Dr. Peter Veneman

Due to the history of wetland loss within the United States a National “No Net Loss” policy was adopted in 1988. This policy requires the creation of mitigation wetlands to replace lost and/or damaged natural wetlands. The role of soil in natural wetland systems is key in providing a number of ecology functions, such as the supply of wetland plant nutrients and the retention of nonpoint source pollutants. Nonetheless, Federal and Massachusetts guidelines regarding the creation of soil and the utilization of organic amendments in mitigation wetlands lack specific parameters and thresholds. This research compares the chemical and physical properties of two commercially available composts and two natural wetland soils and evaluates these materials as possible pollutant sources and sinks.

The results of the characterization study demonstrate significant differences between the compost samples and the wetland soils in regards to the following properties: organic matter content, pH, polarity, total nutrients (P, K, B, Zn, Fe, Al, Cd, Ni, Cr) and extractable nutrients (P, K, Ca, B, Mn). These physio-chemical properties influence the functions of supplying plant nutrients and retaining nonpoint source

pollutants such as excessive nutrients and herbicides. The results of the nutrient release studies indicate that the compost samples behave as potential sources of excessive levels of phosphorus and nitrate. In addition, the pollutant retention studies concluded that the compost samples sorbed lower amounts of phosphorus under aerobic conditions and lower amounts of the commonly-used herbicide, 2,4-D, as compared to the wetland soils.

Overall, the differences in both physio-chemical properties and the behavior of the composts as compared with the wetlands soils as well as each other, substantiate the necessity to re-evaluate Federal and Massachusetts guidelines pertaining to mitigation wetland soil and amendments. Based on the results of this study the following minimal analyses are recommended: organic matter content, pH, total nutrients and extractable nutrients. In addition, based on the phosphorus release and retention studies the following thresholds are recommended to prohibit the release of excessive levels of phosphorus into the mitigation wetland and adjacent aquatic systems: Morgan's extractable P content  $\leq 25 \text{ mg kg}^{-1}$  and/or the total P content  $\leq 1286 \text{ mg kg}^{-1}$ .



## CONTENTS

|   | Page |
|---|------|
| ACKNOWLEDGMENTS.....                                  | v    |
| ABSTRACT.....   | vi   |
| LIST OF TABLES.....                                   | xi   |
| LIST OF FIGURES.....                                  | xiii |
| CHAPTER   |      |
| 1. INTRODUCTION.....                                  | 1    |
| Introduction.....                                     | 1    |
| Justification.....                                    | 2    |
| Hypothesis.....                                       | 5    |
| Objectives.....                                       | 5    |
| Specific Objectives.....                              | 6    |
| 2. LITERATURE REVIEW.....                             | 7    |
| Wetland Inventory & Loss.....                         | 7    |
| Wetland Classification.....                           | 8    |
| Wetland Protection.....                               | 9    |
| Wetland Mitigation Guidelines & Assessment.....       | 11   |
| Wetland Soils.....                                    | 14   |
| Organic Matter.....                                   | 15   |
| Compost.....  | 18   |
| Nonpoint Source Pollution.....                        | 20   |
| Eutrophication.....                                   | 21   |
| Phosphorus & Wetlands.....                            | 23   |
| Redox Potential & Phosphorus Behavior.....            | 24   |
| pH and Phosphorus Behavior.....                       | 27   |
| Organic Matter & Phosphorus Behavior.....             | 29   |
| Phosphorus Sorption Capacity & EPC <sub>0</sub> ..... | 31   |
| Nitrogen & Wetlands.....                              | 34   |
| Wetlands & Nutrient Removal.....                      | 35   |
| 2,4-D.....  | 38   |

|    |  |    |
|----|--|----|
|    | 2,4-D Sorption.....  | 39 |
| 3. | CHEMICAL AND PHYSICAL CHARACTERIZATION OF TWO<br>COMMERCIALLY AVAILABLE COMPOSTS AND TWO ORGANIC<br>WETLAND SOILS..... | 43 |
|    | Introduction.....  | 43 |
|    | Materials.....   | 43 |
|    | Methods.....   | 44 |
|    | Spectroscopic Characterization.....  | 45 |
|    | Results & Discussion.....  | 46 |
|    | pH.....  | 46 |
|    | Percent Organic Matter.....  | 48 |
|    | Total Nutrient Content.....  | 48 |
|    | Extractable Nutrient Content.....  | 51 |
|    | Oxalate Extraction.....  | 54 |
|    | Elemental Analyses.....  | 55 |
|    | ATR-FTIR Characterization.....   | 57 |
|    | <sup>13</sup> CMR NMR Characterization.....  | 59 |
|    | Conclusions.....   | 61 |
| 4. | NUTRIENT RELEASE STUDIES.....  | 63 |
|    | Introduction.....  | 63 |
|    | Materials & Methods.....   | 64 |
|    | Phosphorus Release.....  | 65 |
|    | Saturated Nutrient Release.....  | 66 |
|    | Results & Discussion.....  | 66 |
|    | Phosphorus Release.....  | 67 |
|    | Saturated Nutrient Release.....  | 70 |
|    | Conclusions.....   | 74 |
| 5. | NONPOINT SOURCE POLLUTION RETENTION STUDIES.....   | 76 |
|    | Introduction.....  | 76 |

|   |     |
|---|-----|
| Materials & Methods.....  | 77  |
| Phosphorus Sorption.....  | 78  |
| 2,4-D Sorption.....   | 80  |
| Results & Discussion.....   | 82  |
| Phosphorus Sorption.....  | 82  |
| Aerobic Phosphorus Sorption Maxima.....                           | 82  |
| Anaerobic Phosphorus Sorption Maxima.....                         | 84  |
| Organic Matter.....   | 87  |
| pH.....   | 88  |
| Net Equilibrium Phosphorus Concentration.....                     | 89  |
| Phosphorus Sorption Binding Energy.....                           | 90  |
| 2,4-D Sorption.....   | 90  |
| Conclusions.....  | 94  |
| 6. CONCLUSIONS.....   | 96  |
| Organic Material Characterization.....                            | 96  |
| Nutrient Release Studies.....                                     | 98  |
| Nonpoint Source Pollution Retention Studies.....                  | 99  |
| Recommended Assay For Compost Utilized in Mitigation Wetlands.... | 101 |
| Suggested Future Work.....  | 104 |
| APPENDIX  |     |
| A. PHOSPHORUS SORPTION GRAPHS.....                                | 105 |
| REFERENCES.....   | 111 |

## LIST OF TABLES

| TABLE   | PAGE |
|---|------|
| 2.1. Some Important Functional Groups of Soil Organic Matter (Stevenson, 1982).....   | 17   |
| 2.2. The pH and $S_{\max}$ values for selected wetland soils/sediments.....   | 28   |
| 2.3. The mean total phosphorus $EPC_0$ values of selected wetland soils/sediments.....  | 34   |
| 3.1 Selected physio-chemical properties of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....   | 47   |
| 3.2 Mean total macronutrient of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....  | 50   |
| 3.3 Mean total micronutrient levels of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....   | 50   |
| 3.4 Mean total metal levels of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....   | 52   |
| 3.5 Mean Morgan's extractable macronutrient levels of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....  | 52   |
| 3.6 Mean Morgan's extractable micronutrient levels of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....  | 54   |
| 3.7 Mean Morgan's extractable metal levels of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....  | 54   |
| 3.8 The mean oxalate-extractable iron, aluminum, manganese, and phosphorus concentrations of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> ..... | 55   |
| 3.9 Mean elemental analysis and atomic ratios of 500-micron size fraction of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....                 | 57   |
| 3.10 Mean elemental analysis and atomic ratios of 2-mm size fraction of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....                      | 57   |
| 3.11 Integration of the CPMAS $^{13}\text{C}$ NMR spectra <sup>a</sup> for the two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....               | 61   |
| 5.1 Selected aerobic phosphorus sorption parameters of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....                                       | 83   |
| 5.2 Pearson's correlation values of P sorption attributes with selected soil parameters.....  | 84   |

|   |     |
|---|-----|
| 5.3 Selected anaerobic phosphorus sorption parameters of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> ..... | 86  |
| 5.4 Selected 2,4-D sorption parameters of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....                | 93  |
| 6.1 Pearson's correlation values of 2,4-D sorption $K_f$ with selected soil parameters.....                                 | 102 |
| 6.2 Pearson's correlation values of $\text{PO}_4^{3-}$ release attributes with selected soil Parameters.....                | 102 |

## LIST OF FIGURES

| FIGURE  | PAGE |
|---|------|
| 2.1 Classification hierarchy of wetlands and deepwater habitats, showing Systems, Subsystems, and Classes (Cowardin et al., 1979).....  | 10   |
| 2.2 Schematic diagram of P reactions under oxidized and reduced conditions (Moore and Reddy, 1994).....   | 26   |
| 2.3 Theoretical pe/pH diagram with stability field for strengite and apatite. $pCa^{2+} = 3$ , $pFe^{2+} = 4$ , and $pH_2PO_4^- = 5$ (Moore and Reddy, 1994).....   | 29   |
| 2.4 Direct effects of DOC on P availability (M, metal; LOA, low molecular weight organic acid) (Guppy et al., 2005).....  | 30   |
| 2.5 Sorption isotherm diagram to demonstrate the concepts of net phosphorus equilibrium concentration ( $EPC_0$ ), native adsorbed exchangeable phosphorus (NAP), and maximum phosphorus adsorption capacity (PAC) (Zhou et al., 2005)..... | 33   |
| 2.6 Rates of nitrification, ammonification and denitrification relative to the percentage of water-filled pore space (Brady and Weil, 1999).....  | 35   |
| 2.7 Conceptual diagram of mechanism which contribute to N and P release and exchange in the Lake Apopka constructed marsh (D'Angelo and Reddy, 1994).....   | 38   |
| 3.1 The ATR-FTIR spectra of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....  | 58   |
| 3.2 The solid-state $^{13}C$ NMR spectra of two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....  | 60   |
| 4.1 Orthophosphate release by two composts <sup>†</sup> and two wetland soils <sup>‡</sup> under aerobic conditions.....  | 68   |
| 4.2 Orthophosphate release by two composts <sup>†</sup> and two wetland soils <sup>‡</sup> under anaerobic conditions.....  | 68   |
| 4.3 Orthophosphate release by two composts <sup>†</sup> and two wetland soils <sup>‡</sup> under varying saturation periods.....  | 71   |
| 4.4 Nitrate release by two composts <sup>†</sup> and two wetland soils <sup>‡</sup> under varying saturation periods. ....  | 72   |

|   |     |
|---|-----|
| 4.5 Ammonium release by two composts <sup>†</sup> and two wetland soils <sup>‡</sup> under varying saturation periods.....                    | 74  |
| 5.1 Sorption of phosphorus by a leaf compost under anaerobic conditions for low concentrations of added P (0 to 15 mg L <sup>-1</sup> ). .... | 86  |
| 5.2 Sorption of phosphorus by a leaf compost under anaerobic conditions.....  | 87  |
| 5.3 Logarithmic trends of 2,4-D sorption to two composts <sup>†</sup> and two wetland soils <sup>‡</sup> .....                                | 91  |
| A.1 Sorption of phosphorus by a muck soil under aerobic conditions.....   | 107 |
| A.2 Sorption of phosphorus by a muck soil under anaerobic conditions.....   | 107 |
| A.3 Sorption of phosphorus by a peat soil under aerobic conditions.....   | 108 |
| A.4 Sorption of phosphorus by a peat soil under anaerobic conditions.....   | 108 |
| A.5 Sorption of phosphorus by lobster compost under aerobic conditions.....   | 109 |
| A.6 Sorption of phosphorus by lobster compost under anaerobic conditions.....   | 109 |
| A.7 Sorption of phosphorus by a leaf compost under aerobic conditions.....  | 110 |

## CHAPTER 1

### INTRODUCTION

#### Introduction

Wetlands are defined as those areas that are inundated or saturated by surface or groundwater at a frequency or duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions (33 CFR 328.8(b), 1984). In 1997, there were an estimated 105.5 million acres of wetlands in the conterminous United States, a significant decrease since the pre-settlement estimate of 221 million acres of wetlands (Dahl, 2000). Since wetland inventories first began in the mid-1950's, annual wetland losses have been recorded. Currently, wetlands are protected at federal, state, and local levels. The national policy of "No Net Loss" regarding wetlands was adopted in 1988 to protect wetlands and the valuable functions they provide (National Wetlands Policy Forum, 1988).

Ninety-five percent of the United States' wetlands are freshwater wetlands. Freshwater wetlands include Riverine systems, Lacustrine systems, and Palustrine systems (Cowardin et al., 1979). In addition to encompassing the largest acreage, freshwater wetlands are also subject to the largest losses. In an attempt to decrease wetland losses, federal and state regulations require the mitigation of lost or altered wetlands. Mitigation wetlands must replicate the important functions of the lost or altered wetland. The Wetlands Protection Act of Massachusetts (1972) recognizes the following eight interests served by wetlands: protection of public and private water supply, protection of groundwater supply, flood control, storm damage protection,



protection of land containing shellfish, protection of fisheries, protection of wildlife habitat, and the prevention of pollution (M. G. L. c. 131 § 40).

Non-point source pollution is the leading impairment of the Nation's waters (U.S. EPA, 2000). Non-point source pollutants from agricultural practices include sediment, dissolved nutrients and pesticides. Nitrogen and phosphorus are dissolved nutrients that occur in limited quantities in natural aquatic environments (Brooks et al., 1997). Increased amounts of nitrogen and phosphorus can increase the eutrophication of waterbodies, which in turn reduces dissolved oxygen content and adversely affects aquatic life (Brooks et al., 1997). Toxic pesticides can contaminate waterways and wells, harming wildlife and making drinking water unfit for consumption (U.S. EPA, 2000). While wetlands have long been credited with reducing non-point source pollution, little work exists that examines the mechanisms at work within these systems. As such, the evaluation of mitigation wetlands from the functional standpoint of reducing pollution has been overlooked.

### **Justification**

Since the pre-settlement era, the United States has lost over 50% of its wetlands to activities such as development, agriculture, and roadways (Dahl and Johnson, 1991). As a result of these losses and in an attempt to compensate for them, the United States has adopted a national "No Net Loss" policy regarding wetlands. This policy is supported by local, state, and federal programs. Many of these programs require the creation of replication or restoration wetlands to mitigate for the loss of natural wetlands (Clean Water Act, 1972; Massachusetts Wetland Protection Act, 1972). Guidelines have

been established to aid in the creation of mitigation wetlands; however, the success of mitigation wetlands has been studied and in some cases criticized. Recent studies have shown a lack of in-kind mitigation wetlands. The argument has been made that created wetlands often lack appropriate hydrology, soils, and vegetation and fail to perform the same functions as the lost or altered wetlands they are supposed to replicate (Hashisaki, 1996; Whigham, 1999; Brown and Veneman, 2001). This research increases the body of knowledge pertaining to the chemical and physical properties of both natural wetland soils and mitigation wetland soils with the intent to improve the establishment of in-kind mitigation wetlands in regards to their soil environments.

As discussed in an array of wetland literature, wetlands serve a number of functions (Kusler and Kentula, 1990; Mitsch and Gosselink, 2000). The prevention of pollution, particularly nonpoint source pollution, is a significant function of wetlands that can not be assessed by the successful establishment of a wetland plant community. Several studies have shown that wetland soils and more specifically, their organic matter content have the governing role in a wetland's ability to reduce pollution (Richardson, 1989; Fleischer et al., 1994; Mitsch, 1994). Natural wetlands have been shown to successfully reduce nonpoint source pollution (Kao and Wu, 2001). Constructed wetlands have been utilized to reduce pollution from stormwater runoff (Mitsch et al., 1994; Carleton et al., 2000). Jordan et al. (2003) documented the reduction of nonpoint source pollution in a restored wetland receiving agricultural runoff.

To address the functional success of mitigation wetlands, the role of soil and organic matter within wetland environments needs both consideration and further

study (Maltby, 1986; Veneman, 1986; Lowry, 1990). In his review of freshwater wetland mitigation in the glaciated Northeast, Maltby asserts that "more than any other part of the wetland system, the organic horizon component must be the most difficult to re-create, and for practical purposes this may be regarded as impossible." By carefully evaluating four different organic materials as both potential sources and sinks of nonpoint source pollution within wetland environments, the results of this thesis increase the understanding of the functional role of organic matter within mitigation wetlands.

Although the successful attenuation and/or reduction of nonpoint-source pollution by wetlands has been studied, the characterization of organic matter responsible for reducing pollutants requires more attention. Federal and Massachusetts mitigation guidelines currently allow for the use of organic material amendments to aid in the recreation of "wetland soils". However, both federal and state guidelines provide little specificity as to the appropriate use of amendments. The Army Corp of Engineers currently suggests the use of amendments with high organic matter content and low nutrient levels. The Massachusetts Inland Wetland Replication Guidelines, March 2002, states, "*... if used, soil amendments for the A-horizon consist of equal volumes of organic and mineral materials. No woodchips should be used and organic material should be well or partially decomposed. . .*". These ill-defined guidelines can result in the use of a wide range of organic materials such as peat, compost, and manure. Such materials can vary greatly in their composition and sorption capabilities (Harper and Lynch, 1981; Benoit et al., 1996; Rahn et al., 1999; Gilbert et al., 2004; Tsui and Roy 2007). By assessing the physical and

chemical characteristics of four different organic materials in relation to the release and retention of nonpoint source pollutants, this study aims to contribute to a better assessment of organic amendments for mitigation wetlands.

### **Hypothesis**

The basic premise for this research is that for compost soil amendments to be successfully utilized in wetland replication and restoration projects, those amendments must have similar chemical characteristics to the organic wetland soils being replicated. I hypothesize that commercially available compost materials differ greatly with respect to their chemical and physical composition as compared to natural organic wetland soils and as compared to each other. I further postulate that the ability of soil amendments to supply nutrients for wetland plant growth, to sorb herbicides, and to reduce nutrient levels in water is dependent on the specific nature and composition of the organic material.

### **Objectives**

The overall goal of the study is to compare the composition, nutrient leaching, nutrient retention, and sorption abilities of two commercial composts to that of two naturally occurring organic wetland soils. Such a comparison will allow for the evaluation of composts as organic amendments in wetland mitigation with the goal of replicating the pollution attenuation functions of natural wetland systems.

### **Specific Objectives**

- 1) To measure properties including: pH, macronutrient, micronutrient and trace metal levels (both total and exchangeable), percent organic matter content, and C:N ratio;
- 2) To evaluate the composition of the organic materials via elemental analysis, ATR-FTIR spectroscopy and CPMAS  $^{13}\text{C}$  NMR spectroscopy;
- 3) To determine the effect of initial saturation and periodic anaerobic conditions on the release of nitrogen and phosphorus by organic materials;
- 4) To assess the removal of nitrate under anaerobic conditions;
- 5) To determine the sorption of phosphorus under aerobic and anaerobic conditions; and
- 6) To determine the sorption of the commonly used herbicide, 2,4-D, by organic materials using a batch equilibrium sorption procedure.

## CHAPTER 2

### LITERATURE REVIEW

#### Wetland Inventory & Loss

Prior to the European settlement, 221 million acres of wetland were in existence within the conterminous United States (Dahl and Johnson, 1991). Since that time, wetlands have been lost to filling, dredging, draining, leveling and flooding. The Emergency Wetlands Resource Act of 1986 charged the United States Fish and Wildlife Service with the task of studying and reporting on the Nation's wetland status and trends at 10-year intervals. The Service classifies wetland types according to Cowardin et al. (1979) and employs recent imagery such as aerial photography and direct observations to monitor wetland changes.

The latest published study performed by the Service covers the 10-year interval from 1986 to 1997. According to the report there were an estimated 105.5 million acres of wetland within the conterminous United States in 1997. Of the total acres of wetland, 95% were freshwater wetlands; the largest category was forested freshwater wetlands which encompassed 50.7 million acres (Dahl, 2000).

The estimated total net loss of wetlands from 1986 to 1997 was 644,000 acres. This averages to a loss of 58,500 acres of wetland per year. The majority of wetland losses (98%) were freshwater wetlands. Contributors to wetland losses are, in decreasing order, urban development, agriculture, silvaculture, and rural development. These losses are generally due to permitted actions under Federal and State regulations, after-the-fact permitting, and unprotected non-jurisdictional wetlands (Dahl, 2000).

Several federal, state, and private organizations have worked to reduce wetland loss. Programs implemented under the Food Security Act of 1985 added an estimated 90,000 acres of wetland from 1987 to 1990 (Dahl and Johnson, 1991). While such an addition is an accomplishment, it is still a far cry from the Nation's goal of No Net Loss of wetlands. Likewise, recent studies have questioned whether created wetlands are actually replicating the functions of lost wetlands (Hashisaki, 1996; Whigham, 1999).

### **Wetland Classification**

The first national wetland inventory was conducted by the U.S Fish and Wildlife Service in the early 1950's. The inventory was based on the desire to quantify wetlands from a wildlife habitat perspective, particularly waterfowl. The result was the publication of the U.S. Fish and Wildlife Circular 39. Circular 39 described twenty different types of wetlands, which were each separated into one of four categories: inland fresh areas, inland saline areas, coastal fresh areas, and coastal saline areas. (Shaw and Fredline, 1956).

In the 1970's the U.S. Fish and Wildlife Service began a more meticulous U.S. National Wetlands Inventory. This later inventory modified past inventory methods, broadening the Circular 39 classification to address scientific and management goals. As part of the project, the USFWS recognized the need to adopt a uniform classification of wetland types. This resulted in the publication of The Classification of Wetlands and Deepwater Habitats in the United States by Cowardin et al. (1979), which is now used by the authors of the majority of regulatory and scientific literature (WTI, Inc., 1995; Dahl,

2000; MADEP, 2002). Classification of Wetlands and Deepwater Habitats of the United States, classifies wetlands according to vegetation, soils, and hydrology into five major Systems: Marine, Estuarine, Riverine, Lacustrine, and Palustrine. Wetland systems are then further divided into Subsystems, Classes, Subclasses, and Dominance Types (Figure 2.1).

According to Cowardin et al., “The Palustrine system includes all nontidal wetlands dominated by trees, shrubs, persistent emergents, emergent mosses or lichens...”. Palustrine systems are wetlands commonly known as bogs, swamps, fens, forested wetlands, and wet meadows, many of which fall under jurisdictional regulations. Those Palustrine systems adjacent to rivers, streams, lakes, and ponds, have been recognized as filters that improve the quality of neighboring waterbodies (Gilliam, 1994).

### **Wetland Protection**

A majority of wetlands are protected by both federal and state regulations, or by private programs. On a federal level, wetlands are protected as “waters of the United States” under the Clean Water Act Section 404 of 1972. Under the Clean Water Act, proposed wetland alterations such as dredging and filling require permitting by the U.S Army Corps of Engineers. To aid in the protection of wetlands as a valuable resource, the permitting process must evaluate proposed wetland alterations according to a three step sequence: 1) the extent to which adverse impacts can be *avoided*, 2) the extent to which adverse impacts are *minimized* and 3) the extent to which *mitigation* measures, including replication or restoration, are provided.



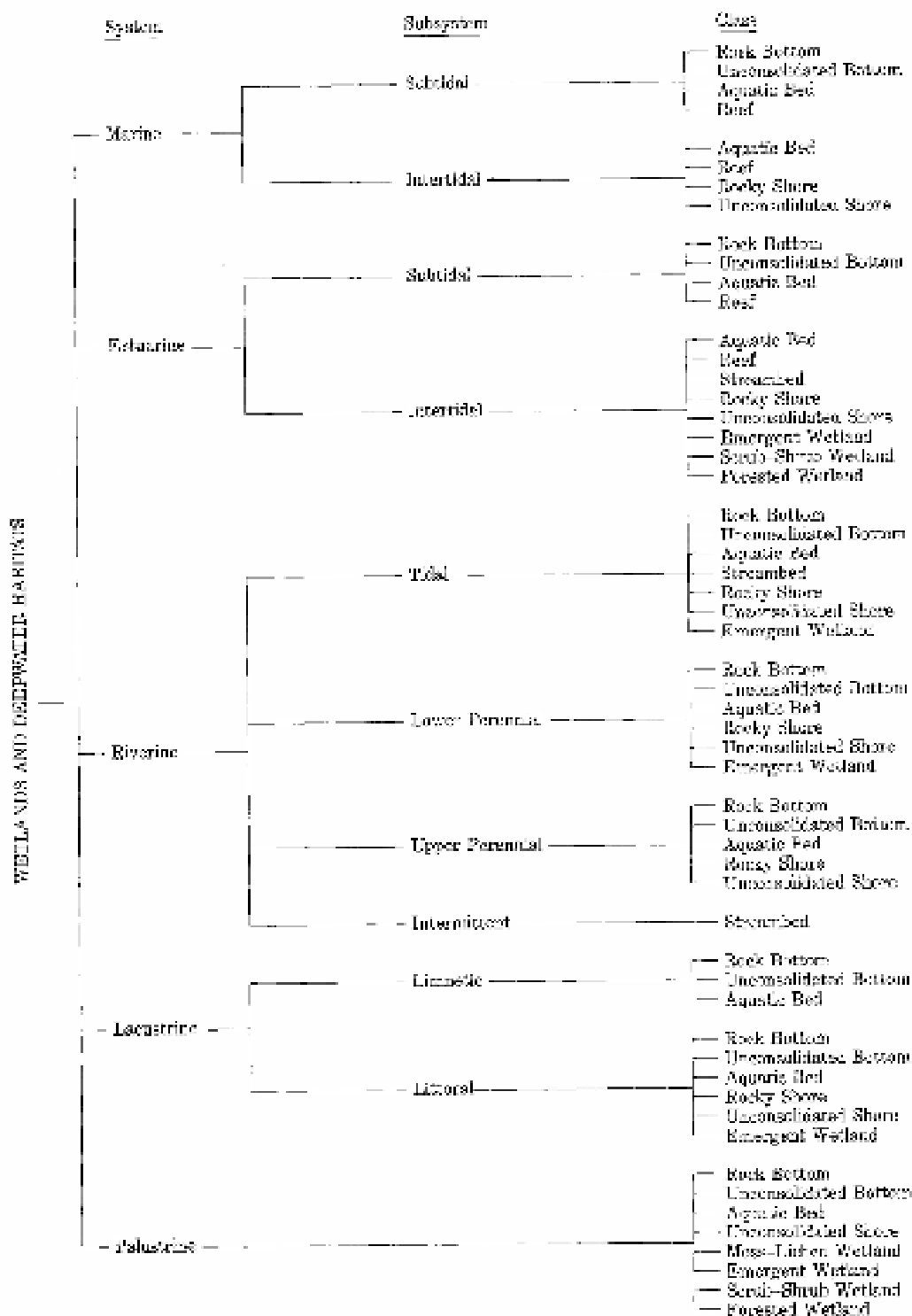


Figure 2.1. Classification hierarchy of wetlands and deepwater habitats, showing Systems, Subsystems, and Classes (Cowardin et al., 1979).

On a state level, 16 states have established wetland protection regulations (Mitsch and Gosselink, 2000). In the Commonwealth of Massachusetts, wetland protection is governed by a particularly stringent set of regulations. One of the objectives of the Massachusetts Wetlands Protection Act (M.G.L. Ch. 131§40) is “No Net Loss” of wetlands, a concept which was also adopted on a federal level in 1988 under the National Wetlands Policy. Wetland regulations in the Commonwealth of Massachusetts allow for certain limited wetland alterations. Based on “No Net Loss”, allowable wetland alterations must be replicated. General performance standards for wetland replication are listed under 310CMR 10.55(4) and include such standards as a minimal 1:1 (impact area to replication area) ratio, the establishment of 75% cover of wetland indicator plant species within two years, and the implementation of similar hydrology to the altered wetland.

In the state of Massachusetts, the Wetlands Protection Act is administered by volunteer town residents appointed to serve on the Conservation Commission. In addition to administering the state regulations, Conservation Commissions often administer local wetland bylaws that have been passed by their town or city. The Massachusetts Association of Conservation Commissioners reports that 351 cities and towns have adopted local wetland bylaws (Dawson and Zielinski, 2002). Local bylaws usually institute a greater level of wetland protection.

### **Wetland Mitigation Guidelines & Assessment**

In recent years, the success of wetland replication projects has been studied and in some cases criticized (Hashisaki, 1996; Whigham, 1999; Brown and Veneman, 2001).

The argument has been presented that the success of a wetland replication should depend on more than simply the establishment of wetland plant species within a specified area (Whigham, 1999). Few studies have addressed the role of soils in mitigation wetlands; and these have merely assessed the success of translocating natural wetland soils and/or adding organic amendments (leaf litter) in mitigation areas on the ability of these soil types to support wetland plant life and diversity (Stauffer and Brooks, 1997; Brown and Bedford, 1997). Such an assessment neglects the other functional aspects of wetland soils.

To ensure that the functions of the altered or lost wetland have been successfully replicated, the replicated wetland must also perform the same or similar functions as the altered or lost wetland. Wetland functions are dependent not only on vegetation, but also on the hydrology and soils associated with an individual wetland. Wetland functions include ground water recharge and discharge, flood storage, erosion and shoreline anchoring, sediment trapping, nutrient retention and removal, food chain support, fisheries and wildlife habitat, and recreation and heritage value (Adamus, 1983; Mitsch and Gosselink, 2000). Very little work exists that has examined the “functional” success of mitigation wetlands. One such study identified differences between constructed wetland soils and an adjacent Palustrine reference wetland soils (Stolt et al., 2000). Important soil characteristics such as water-table level, soil temperature, redox potential and organic matter content were concluded to differ, suggesting that wetland functions may not have been replaced to the same capacity as the original wetland.

Brown and Veneman (2001) reviewed the effectiveness of compensatory wetland mitigation in Massachusetts. The study concluded that 54% of the 114 field sites failed to meet the Massachusetts regulations for wetland mitigation. The largest cause was a failure to attempt replication (which demonstrates a lack of sufficient regulatory oversight). Other causes of mitigation failure included the lack of in-kind replication and insufficient hydrology and vegetation. In-kind replication refers to the goal of recreating the same wetland system type (i.e. if the wetland to-be-altered is a forested red maple swamp the replication wetland should be a forested red maple swamp, not a cattail marsh). The hydrology of the replication wetland must be sufficient to provide saturated and/or inundated soil conditions for a significant period of the growing season and the replication area must contain a minimum of 75% coverage of indigenous wetland plant species within two growing seasons to meet the performance standards stated in the Massachusetts Wetlands Protection Act Regulations (2005). Following the Brown and Veneman (2001) study, the Massachusetts Department of Environmental Protection published the Massachusetts Inland Wetland Replication Guidelines, in March 2002 (MADEP, 2002). The guidelines serve to support the “No Net Loss” objective and provide Conservation Commissions with information on the necessary hydrology, vegetation, and soil parameters for a successful wetland replication. Both the Massachusetts’ and the Army Corps of Engineers’ wetland replication guidelines address the importance of soil and organic matter. However, neither is specific as to the appropriate use and type of soil amendments. Guidelines recommend the use of soil amendments that are uncontaminated, have low nutrient contents, and are well or

partially decomposed, but do not address how different soil amendments will function as compared to natural wetland soils.

### **Wetland Soils**

“A hydric soil is a soil that formed under conditions of saturation, flooding, or ponding long enough during the growing season to develop anaerobic conditions in the upper part.” (WTI, Inc., 1995). Hydric soil characteristics are affected by all soil forming factors (time, parent material, organisms, relief, and climate) but most predominately by the hydrological regime (WTI, Inc., 1995). Under saturated soil conditions, oxygen diffusion declines by  $10^4$  times compared to oxygen diffusion through a porous medium (Maltby, 1986). As a result saturated soils become chemically reduced. In the absence of oxygen, microbial processes must use different electron acceptors. Inorganic compounds are then reduced as follows: nitrate, manganese, iron, sulfur, carbon dioxide. Anaerobic conditions decrease the microbial decomposition of organic matter, thus allowing for a significant accumulation of organic matter within the upper part of a soil.

Hydric soils can be separated into two major categories: organic soils and mineral soils. Most soils contain some organic matter, however, those soils which contain greater than 20% to 35% organic matter are generally considered organic. Organic soils are defined by criteria set forth by the USDA, Soil Survey staff. Sandy soils without any clay and with 20% or more organic matter (12% or more organic carbon), or fine-textured soils with 60% or more clay and 30% or more organic matter (18% or more organic carbon) are defined as organic soils (Soil Survey Division Staff, 1993).

Taxonomically, organic soils are classified as Histosols. Within the order of Histosols, organic soils are further classified into suborders: Folists, Fibrists, Hemists, and Saprists (Soil Survey Staff, 2003). Folists are organic soils located in boreal and tropical climates. Folists are saturated with water for less than 30 consecutive days and therefore are not considered hydric soils (Soil Survey Staff, 2003). Fibrists organic soils are comprised of peat material. Peat is defined as organic remains that are sufficiently fresh and intact to permit identification of plant parts. Saprists organic soils are comprised of muck. Muck is defined as organic remains that are highly decomposed and do not permit the identification of plant parts. Hemists organic soils are comprised of mucky peat. Mucky peat describes organic remains of which a significant amount, but not all, of the plant parts can be identified (Soil Survey Division Staff, 1993). Fibrists, Saprists, and Hemists are considered hydric soils.

### **Organic Matter**

Organic matter is a predominant characteristic of wetland soils, whether as the parent material of organic soils or as a significant component of mineral wetland soils. As a predominant soil characteristic, organic matter content and quality influences a number of physical, biological, and chemical properties in wetland soils. Organic matter has a high, pH dependent cation exchange capacity. As pH increases, organic matter develops an increased negative charge, thus increasing cation exchange capacity. As pH decreases, organic matter develops an increased positive charge, thus increasing anion exchange capacity (Tan, 1998). Increased anion exchange capacity may enhance plant growth through the sorption of anionic toxic pollutants such as herbicides and the

retention of exchangeable nutrients such as  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ . Organic matter has a high water holding capacity, which may perpetuate the saturated conditions that enhanced organic matter accumulation. Although generally slower in wetland systems as compared to oxygenated uplands, mineralization of organic matter yields  $\text{CO}_2$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$ , thus creating a source for plant nutrients.

In addition to providing essential elements for wetland plant growth, organic matter has a predominant role in the fate of toxic substances in the environment; organic matter chelates with heavy metals like Pb,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Zn}^{2+}$ , forming stable complexes (Stark et al., 1994; Färm, 2002). Organic pollutants such as pesticides have a strong affinity for organic matter. The retention of organic pollutants by organic matter results from adsorption on humic substances (Koskin and Harper, 1990) and is dependent on the physiochemical properties of the pollutant as well as the presence of certain humic substance functional groups (Sparks, 1995). Important functional groups of soil organic matter are illustrated in Table 2.1.

Organic matter in soils consists of the living carbonaceous fraction (biomass), unaltered or partially decomposed organic debris, and humus, highly stable substances derived from the decomposition of plants, animals, and microorganisms. Humus can be further classified into recognizable compounds or amorphous polymers (Hayes, 1983). Recognizable compounds, also known as non-humic substances, include carbohydrates, proteins, lipids, and waxes. Amorphous polymers or humic substances include humic acids, fulvic acids, and humin. Humic substances have relatively high molecular weights and are formed by secondary synthesis reactions (Brady and Weil, 1999).

Table 2.1. Some important functional groups of soil organic matter (Stevenson, 1982).

| Functional group      | Structure      |
|-----------------------|----------------|
| <b>Acidic groups</b>  |                |
| Carboxyl              | $R-C(=O)-OH$   |
| Enol                  | $R-CH=C(H)-OH$ |
| Phenolic OH           | $Ar-OH$        |
| Quinone               | $Ar=O$         |
| <b>Neutral groups</b> |                |
| Alcoholic OH          | $R-CH_2-OH$    |
| Ether                 | $R-O-CH_2-R'$  |
| Ketone                | $R-C(=O)-R'$   |
| Aldehyde              | $R-C(=O)-H$    |
| Ester                 | $R-C(=O)-OR'$  |
| <b>Basic groups</b>   |                |
| Amine                 | $R-CH_2-NH_2$  |
| Amide                 | $R-C(=O)-NH_2$ |

The characterization of humic substances based on solubility has proven to give limited insight on chemical behavior (Brady and Weil, 2002) and as such the practice of Carbon 13 Nuclear Magnetic Resonance ( $^{13}C$  NMR) and Fourier Transform Infrared Spectroscopy (FTIR) analyses has risen in recent years.  $^{13}C$  NMR spectroscopy is an advantageous non-destructive tool in the characterization of organic materials. This method permits the analysis of solid organic materials and aids in the identification of organic structures present in the sample (Kögel- Knabner et al., 1997). Structural differences between organic materials can be determined by changes in the shape and intensity of peaks within the NMR spectrums. FTIR spectroscopy is a non-destructive method used to identify the functional groups within an organic material sample. The FTIR spectroscopy is used in conjunction with a second analytical tool (such as NMR) to determine the complete structure of a given sample (Smith, 1996).



## Compost

Unlike the decomposition of organic matter in natural environments, composting can be defined as the microbial reduction of organic wastes into humic-like substances outside of the natural soil environment (Barker, 1997). Composts consist of organic residues, or a mixture of organic residues and soil that have been amassed, moistened and allowed to undergo biological decomposition. Brady and Weil (1999) define the production of compost as a three-step process (mesophilic stage, thermophilic stage, and second mesophilic stage), under conditions conducive to aerobic decomposition and nutrient conservation. This engineered practice differs from the slow anaerobic decomposition within natural wetland environments. During the composting process: the amount of nonhumic substances decline and the humic substances content increases; the C/N ratio decreases and stabilizes in a range from 14:1 to 20:1; and the cation exchange capacity of initial organic materials increases to about 50 to 70 cmol kg<sup>-1</sup> (Barker, 1997; Brady and Weil, 1999).

Composting originates from an agricultural background and has involved a variety of organic materials such as leaf litter, manures, food wastes, weeds, logging and wood manufacturing wastes, and biosolids (Barker, 1997). The resulting products have been conventionally used in potting soil mixes, as mulch, and as slow-release fertilizer. Additionally, composting has been used as a method to reduce and treat organic wastes (Haug, 1993). In more recent years, composts have been used as soil amendments in wetland creation (Stark et al., 1994; Jarvis and Young, 1999).

Spent mushroom composts (comprised of horse manure, dried straw, chicken manure, dried brewer's grain, gypsum, rye grain spawn, peat moss, and ground limestone) have been commonly used in constructed wetlands to treat coal mine drainage, successfully retaining iron (Stark et al., 1994). A full-scale compost wetland containing cattle manure, horse manure, municipal waste compost, and limestone successfully removed 45% of the iron and 63% of the aluminum from acid mine drainage after a twelve-month period (Jarvis and Young, 1999). The reduction of stormwater Cr, Cu, and Zn has been achieved via sorption by natural filter substrates, burnt opoka and peat (Färm, 2002). Orhan and Büyükgüngör (1993) studied the removal of Cr(VI), Cd(II), and Al(III) using different agricultural adsorbents. Five adsorbents (waste tea; Turkish and exhausted coffee; nut and walnut shells) demonstrated high adsorption capacities for Cr(VI), Cd(II), and Al(III).

Recent studies have documented the use of compost in the creation of wetlands, for both restoration and mitigation projects. The Departments of Transportation in 30 states have reported using compost in wetland mitigation projects associated with construction (BioCycle, 2002a). In the state of New Hampshire, 20,000 cubic yards of yard trimmings compost was used to restore a superfund site (BioCycle, 2002b). A study conducted in Everett, Washington concluded that biosolid and yard waste compost was successful in mimicking wetland soils by protecting surface waters from the overload of nitrogen and contaminants and by preventing ammonia N transport (Peot, 1997). Both biosolid/yard waste and yard waste composts have been utilized in

the restoration of damaged wetlands in the Seattle, Washington area (Peot and Thompson, 1996; BioCycle, 1996).

It is important to note, that although the utilization of composts in wetland creation has been greatly implemented and reported, these articles have not supplied consistent scientific analysis of either compost composition or wetland value and functional replication success.

### **Nonpoint Source Pollution**

A predominant public interest served by wetland function is the prevention of pollution (MADEP, 2002), through sediment trapping, retention and removal of chemical contaminants such as pesticides and heavy metals, and the storage and transformation of nutrients such as nitrogen and phosphorus (D'Angelo and Reddy, 1994; Kao and Wu, 2001,). These pollutants commonly enter the environment as what is known as nonpoint source pollution.

Nonpoint source pollution (NPS) is pollution from urban and agricultural land that is transported by precipitation and runoff (U.S. EPA, 2000). According to the 2000 National Water Quality Inventory, prepared under Section 305(b) of the Clean Water Act, nonpoint source pollution is a leading issue affecting the nation's impaired waters (U.S. EPA, 2000). More specifically, siltation, nutrients, bacteria, metals and oxygen-depleting substances are among the top causes of impairment.

States, tribes, territories and interstate commissions reported to the EPA in 2000 that approximately 50% of estuaries, 45% of lakes and 40% of streams were not clean enough to provide activities such as swimming and fishing. Nonpoint source pollution

is primarily responsible for the impairment of these waterways. Agricultural NPS pollution is considered a principal cause of environmental contamination, most notably the decrease in our nation's water quality. Agricultural NPS pollution constituents include dissolved nutrients, pesticides and sediments.

Due to their generally low landscape position, wetlands often are subject to activities (agricultural or urban) that occur on adjacent upland areas. Run-off, sedimentation transport, and drainage from upland areas move down gradient to low positions in the landscape. Wetlands adjacent to agricultural areas have been studied from two major perspectives: 1) wetland protection, and 2) water quality. Wetlands situated between agricultural upland areas and waterways have been studied and their effectiveness in removing nutrients and sediments has been demonstrated (D'Angelo and Reddy, 1994; Gilliam, 1994; Woltemade, 2000; Kao and Wu, 2001; Jordan et al., 2003).

### **Eutrophication**

Eutrophication is defined as the process of nutrient enrichment leading to dense algal growth in streams and lakes (Brooks et al., 1997). When levels of limiting essential nutrients such as phosphorus and nitrogen are increased, bacterial populations increase which causes higher respiration rates and ultimately hypoxia or anoxia (Correll, 1998). Hypoxia is an environmental condition where dissolved oxygen levels are  $<2.0 \text{ mg L}^{-1}$  (Mitsch and Gosselink, 2000). Anoxia is an environmental condition where oxygen is absent, also described as an anaerobic condition. Low dissolved oxygen in waterways leads to a loss of aquatic life, biodiversity, and the release of additional limiting nutrients, which then fortifies eutrophication.

Nitrogen, generally as ammonium or nitrate, is a dissolved nutrient responsible for accelerated rates of eutrophication in surface waters. High concentrations of nitrate alone can lead to eutrophication. Whereas, in the presence of phosphorous, smaller amounts of nitrate, ( $0.30 \text{ mg L}^{-1}$ ), can result in algal blooms (Brooks et al., 1997). In addition, high levels of nitrate (exceeding  $10 \text{ mg L}^{-1}$ ) in drinking water can have serious human side effects, causing illness such as blue baby syndrome (methemoglobinemia) (U.S. EPA, 1986).

Phosphorus (P), a mineral nutrient, is a component of several biological compounds such as nucleoside triphosphates and nucleic acids, and has a predominant role in biochemical reactions. Owing to metal fixation (i.e. Fe, Al, Ca, and Mg), phosphorus often has a low bioavailability in upland agricultural systems. As a result, phosphorus fertilizers and manures are often applied to agricultural soils in relatively heavy amounts and may result in nonpoint source pollution of waterways. Phosphorus is a limiting nutrient in many waterways. When increased amounts of phosphorus enter waterways, the eutrophication process can be accelerated (Brady and Weil, 1999). While there are currently no federal limits on phosphorus levels, the U.S. EPA recommends that total P entering lakes or reservoirs should not exceed  $0.1 \text{ mg L}^{-1}$  (U.S. EPA, 1986).

A review published by Ryden et al. (1973) stated “Increasing evidence suggest that P in surface waters is the primary factor controlling the eutrophication of surface water supplies.” For over 30 years the transport, release, environmental concerns, and management practices regarding phosphorus have been studied (Sims et al., 1998). Due

to phosphorus fixation in the soil, many studies have examined phosphorus concentrations in waterways from sediment transport, surface erosion, and runoff (Gilliam, 1994; Woltemade, 2000; Kao and Wu, 2001). In addition, phosphorous can enter surface waters in soluble form through leaching and subsurface runoff. Certain environmental factors such as chemically reducing conditions, sandy soils, and over-fertilization can increase the transfer of phosphorus into soluble forms (Sallade and Sims, 1997b; Sims et al., 1998).

### **Phosphorus & Wetlands**

Traditionally, wetlands have been attributed with the reduction of phosphorus as a nonpoint source pollutant. However, recent studies have indicated that the anaerobic conditions present in wetland systems may lead to high phosphorus bioavailability (Patrick and Khalid, 1974; Khalid et al., 1977; Pant and Reddy, 2001). Unlike other plant nutrient cycles, P is not removed from wetland environments via a gaseous stage (Richardson and Vepraskas, 2001). As such, P retention by wetlands is limited. The unique landscape position of wetlands between upland and aquatic systems requires an increase in the understanding of phosphorus sorption mechanisms within wetland environments. Sorption capabilities of wetland soils and sediments have been correlated with properties such as, metal speciation and concentration, pH, percent organic matter, wet-dry cycles, and redox chemistry (Appelt et al., 1975; Moore and Reddy, 1994; Pant and Reddy, 2001).

Phosphorus exists in wetland systems in three predominant forms: orthophosphates, fixed mineral phosphorus, and organic P. Orthophosphates are the

pH dependent anionic form of P and include  $\text{H}_2\text{PO}_4^{1-}$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ , which exist at pH ranges of 2 to 7, 8 to 12, and >13, respectively (Richardson and Vepraskas, 2001).

Fixed mineral P consists of orthophosphate anions that are bound to cations, such as Ca, Mg, or oxides and hydroxides containing Fe, Al, and Mn. Organic P located in soils and sediments include: partially decomposed plant tissue; decaying microbes; and orthophosphate anions bound to humic acids, fulvic acids, and low molecular weight organic acids. Organic P comprises >95% of the total P in organic wetland soils.

### **Redox Potential & Phosphorus Behavior**

Phosphorus has a constant positive valence of 5 that is not subject to redox processes. However, P chemistry in wetland systems is indirectly affected by redox processes via the relationship between P, Fe, and Mn. Under low redox potential conditions, there is an increase in both solution P and Fe (Holford and Patrick, 1979). This increase has been attributed to the dissolution of both amorphous and crystalline  $\text{Fe}^{3+}$  phosphate minerals as ferric iron ( $\text{Fe}^{3+}$ ) is reduced to ferrous iron ( $\text{Fe}^{2+}$ ) (Moore and Reddy, 1994) (Figure 2.2). Studies have demonstrated a positive correlation between P sorption and amorphous  $\text{Fe}^{3+}$  oxides and hydroxides (Richardson, 1985; D'Angelo and Reddy, 1994; Reddy et al., 1998, Hogan et al., 2004). Amorphous ferrous hydroxides have a greater surface area and number of sorption sites than crystalline ferric compounds, and may be formed from a secondary precipitation, depending on pH (Holford and Patrick, 1979). The net quantity of solution P is dependent on the balance of P released as iron phosphates dissociate and the amount of P sorbed by newly precipitated amorphous iron hydroxides. Studies have demonstrated that the P sorption

maxima for wetland soils are greater under aerobic conditions as compared to anaerobic conditions (Reddy et al., 1998; Pant and Reddy, 2001). Data presented by Litaor et al. (2005) concurred with previous studies at low concentrations of added P ( $< 8.0 \text{ mg L}^{-1}$ ), where the sorption maximum was higher for aerobic samples. However, at high concentrations of added P ( $70.0 \text{ mg L}^{-1}$ ), the sorption maximum of anaerobic samples was reportedly higher than the aerobic samples. Litaor et al. (2005) attributed the higher anaerobic phosphorus sorption predominantly to Ca-P precipitation during the experiment as well as to the potential re-adsorption of P on organometallic complexes and the sorption on Al-oxides, which are unaffected by redox. Moore and Reddy (1994) also concluded that Ca-bound P was higher under reducing conditions whereas, Fe most likely controlled solution P under oxidizing conditions.

P fixation by Al, Ca and Mg, is not affected by redox, as these metals do not participate in redox reactions. However, the solubility of these P-metal complexes is dependent on pH.



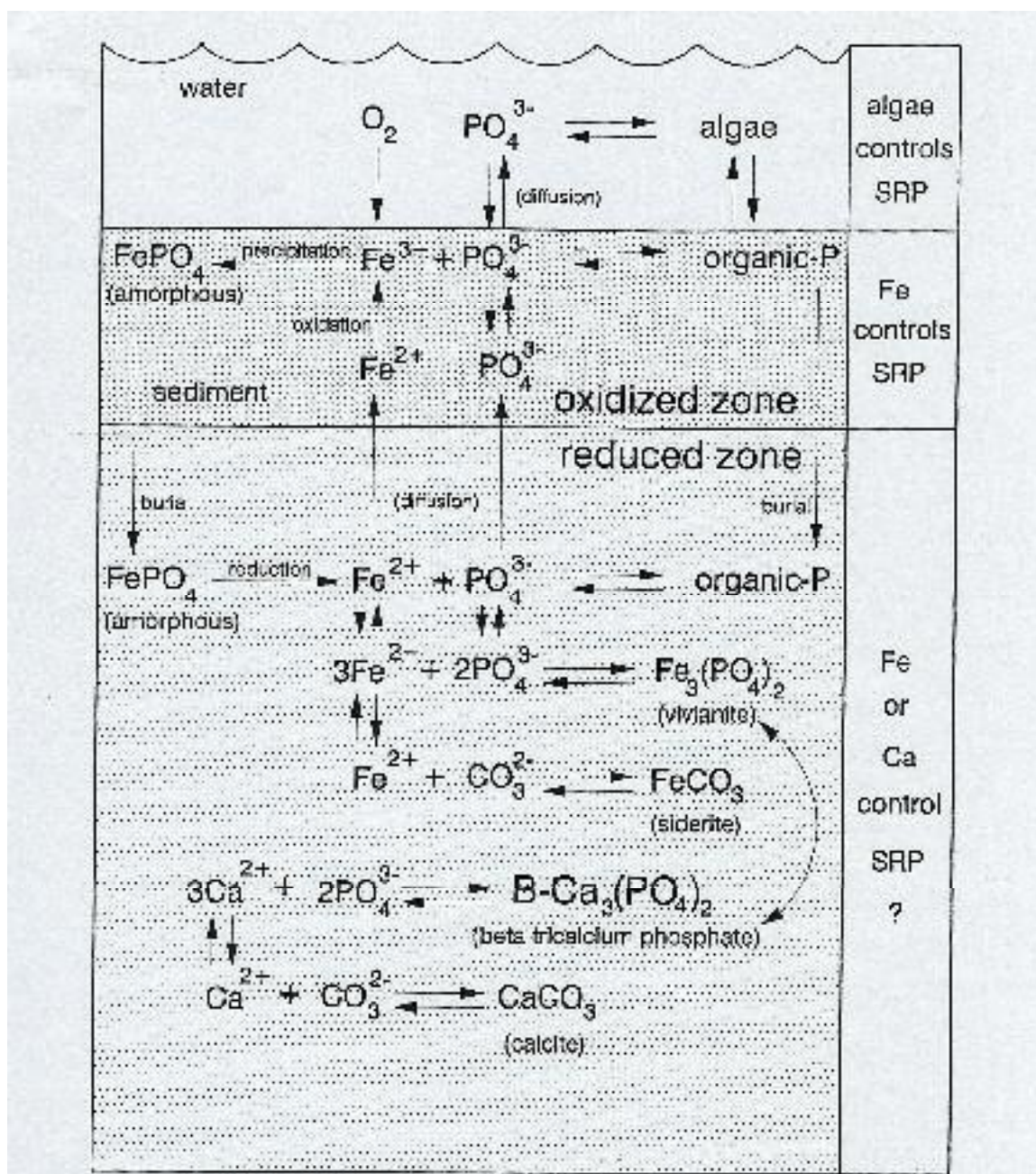


Figure 2.2. Schematic diagram of P reactions under oxidized and reduced conditions (Moore and Reddy, 1994).

## **pH & Phosphorus Behavior**

The fixation of P by metals is pH dependent. In highly acidic soils, such as those found in bogs (pH values  $\leq 4$ ), Fe and Al oxides and hydroxides dissolve, which results in a release of previously sorbed P into solution. At pH values between 4 and 7, amorphous Fe and Al oxides and hydroxides are present and may readily sorb P, resulting in a decrease in solution orthophosphates. At pH values greater than 7, P sorption is predominantly governed by Ca, Mg, and carbonates (Richardson and Vepraskas, 2001). In alkaline, arid soils, P may form insoluble complexes with Ca (apatite) or Mg. The pH of wetland systems also affects the concentration of organic acids, which may compete with P for sorption sites. Table 2.2 illustrates the various pH and sorption maximum ( $S_{\max}$ ) values for different wetland soils/sediments, as published in the literature. The sorption maximum is the total amount of phosphorus that can be sorbed onto the sorbent.

Mildly acidic soils have been reported to sorb significantly higher amounts of P than alkaline soils (Olsen and Watanabe, 1957). In addition, mildly acidic soils also have a reportedly higher  $k$  value (binding energy) than alkaline soils, thus indicating that in addition to sorbing more P, acidic soils/sediments also retain more sorbed P than alkaline soils/sediments (Olsen and Watanabe, 1957; Stumm and Morgan, 1996). Greater retention may be attributed to the sorption of P by Al and Fe oxides and subsequent binuclear bridging, which produces more stable complexes than precipitation and anion exchange reactions.

Table 2.2. The pH and total phosphorus  $S_{\max}$  values for selected wetland soils/sediments.

| Sample                   | pH        | $S_{\max}$ (mg kg <sup>-1</sup> ) | Study                     |
|--------------------------|-----------|-----------------------------------|---------------------------|
| Clay                     | 7.0-7.9   | 246                               | Olsen and Watanabe, 1957  |
| Silt loam                | 7.0-7.9   | 127                               | Olsen and Watanabe, 1957  |
| Aerobic Sediment I-4     | 8.1       | 85.5                              | Pant and Reddy, 2001      |
| Aerobic Sediment I-11    | 7.2       | 500                               | Pant and Reddy, 2001      |
| Aerobic deep Histosol    | 7.2 ± 0.3 | 1400 ± 350                        | Litaor et al., 2005       |
| Aerobic shallow Histosol | 6.8 ± 0.4 | 1110 ± 90                         | Litaor et al., 2005       |
| Silty clay loam          | 5.6       | 769                               | Siddique & Robinson, 2003 |
| Silt loam                | 5.9       | 278                               | Siddique & Robinson, 2003 |
| Silt loam                | 5.9       | 192                               | Siddique & Robinson, 2003 |
| Silt loam 65mV           | 5.0       | 387                               | Holford and Patrick, 1979 |
| Silt loam 65mV           | 6.5       | 392                               | Holford and Patrick, 1979 |
| Silt loam 65mV           | 8.0       | 787                               | Holford and Patrick, 1979 |
| Aerobic Rucks wetland    | 4.1       | 213                               | Reddy et al., 1998        |

Patrick and Khalid (1974) reported that under anaerobic conditions, the solubility of Fe<sup>2+</sup> phosphates decreased with increasing pH when enhanced by newly precipitated Fe(OH)<sub>2</sub> occurring at pH 6.5. Khalid et al. (1977) reported no apparent precipitation of Fe(OH)<sub>2</sub> at pH value <6.4. Moore and Reddy (1994) indicated reduced sorption and extremely high soluble P levels under reducing (Eh<0mV) and acidic (pH 5.5) conditions and low soluble P levels under circum neutral conditions (pH 6.5 and 7.5) (Figure 2.3). High concentrations of soluble P were attributed to the dissolution of ferric phosphates such as strengite (FePO<sub>4</sub> · 2H<sub>2</sub>O). The pH of soil and sediments adjusts towards neutral with anaerobiosis (Mitsch and Gosselink, 2000; Richardson and Vepraskas, 2001).

Therefore, the majority of freshwater wetland systems have water chemistries that are circumneutral, thus accommodating P release in the absence of calcium.

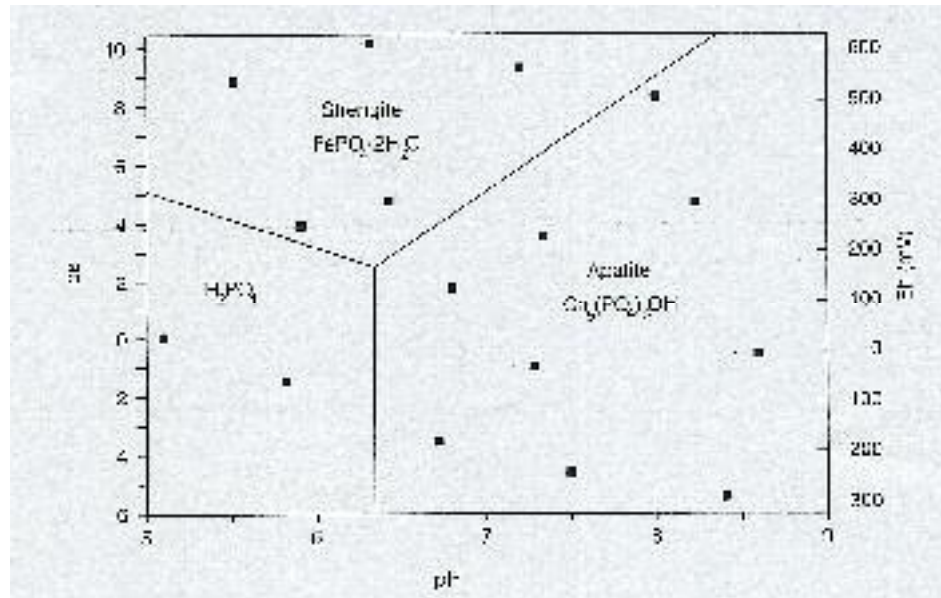


Figure 2.3. Theoretical pe/pH diagram with stability field for strengite and apatite.  $pCa^{2+} = 3$ ,  $pFe^{2+} = 4$ , and  $pH_2PO_4^- = 5$  (Moore and Reddy, 1994).

### Organic Matter & Phosphorus Behavior

Organic matter has several potential direct effects on phosphorus sorption. The decomposition of organic matter releases carbon compounds. Dissolved organic carbon (DOC) can either enhance or decrease phosphorus sorption by soils, depending on whether the dominant interaction involves metal bridging, sorption, or anionic exchange. As illustrated in Figure 2.4, Low Molecular Weight Organic Acids (LOAs) can bind phosphorus via metal bridging (i.e. Ca, Mg, Fe, Al). Metal bridging increases sorption sites, thus decreasing phosphorus in solution (Owusu-Bennoah and Acquaye, 1989; Guppy et al., 2005).

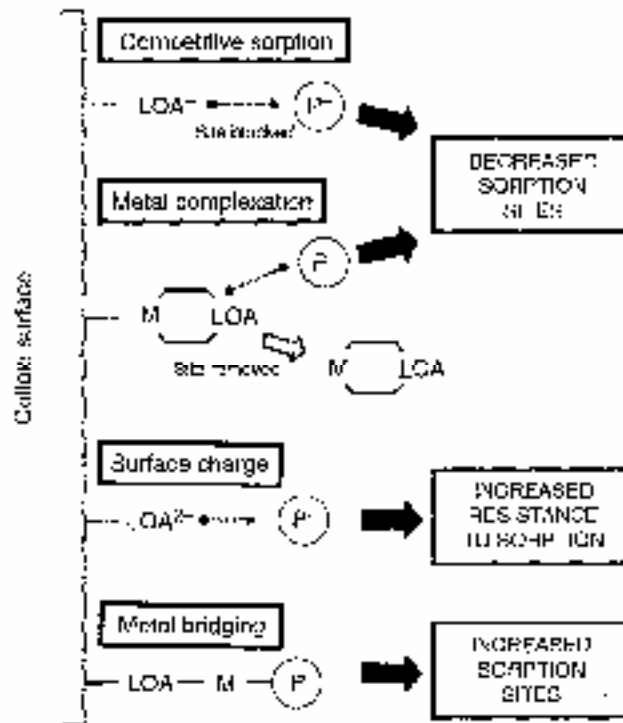


Figure 2.4. Direct effects of DOC on P availability (M, metal; LOA, low molecular weight organic acid) (Guppy et al., 2005)

Competitive sorption of LOAs has a predominate role in the concentration of P in the soil solution. Both P and LOAs are multiprotonic anions and therefore the charge and species in solution are pH dependent. The low pKa values of several LOA (i.e. acetate, lactate, and formate) indicate that sorption increases with decreasing pH; therefore, competitive sorption of P would increase with decreasing pH (Guppy et al., 2005). Other factors contributing to the competitive sorption of LOAs include: LOA type (tricarboxylic > dicarboxylic > monocarboxylic) (Lopez-Hernandez et al., 1986), stability of LOA-metal complexes, and the presence of oxides (Bar-Yosef, 1996). As is the case with P sorption, LOA sorption is associated with sesquioxides (Fe, Al, Mn) and relative affinity for mineral surfaces (amorphous aluminum > ferrihydrite > goethite) (Jones and

Brassington, 1998; Kaiser and Zech, 1998). High molecular weight DOC (humic acids and fulvic acids) may also compete with P for sorption sites; competition increases with decreasing pH (Heng, 1989).

Studies have indicated that the rewetting of wetland soils has an effect on turbidity, DOC, and pH (Elkbatib, 1990; Baziramakenga et al., 1995; Qui and McComb, 2002). Wetland dry cycles enhance organic matter decomposition. Ensuing wet cycles may then lead to increased DOC concentrations and turbidity. Thus, wetlands that undergo periods of wet and dry cycles are susceptible to releases of LOAs and subsequent higher levels of solution P.

### **Phosphorus Sorption Capacity & EPC<sub>0</sub>**

Phosphorus sorption was first successfully fitted to the Langmuir isotherm model by Olsen and Watanabe (1957). The phosphorus sorption capacity can be calculated using the Langmuir isotherm model:

$$S_T = S_0 + (kS_{max}C_t)/(1 + kC_t)$$

where  $S_{max}$  is the maximum amount of phosphorus adsorbed ( $\text{mg kg}^{-1}$ ),  $S_0$  is the initial P present in the adsorbed phase ( $\text{mg kg}^{-1}$ ),  $S_T$  is the total amount of adsorbed P ( $\text{mg kg}^{-1}$ ),  $C_t$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ), and  $k$  is a binding energy constant ( $\text{L mg}^{-1}$ ).

Describing P sorption with the Langmuir model has an advantage over the Freundlich and linear models in that the Langmuir equation can be used to obtain the phosphorus sorption maximum ( $S_{max}$ ) and net equilibrium phosphorus concentration (EPC<sub>0</sub>).

Unlike sorption studies conducted for chemical pollutants (herbicides, pesticides, polycyclic aromatic hydrocarbons), P sorption studies must account for initial concentrations

of P within the sorbent. Olsen and Watanabe (1957) concluded that Langmuir constants ( $b$ , sorption max and  $k$ , bonding energy) were affected by the correction for initial P concentrations. Initial P concentrations can be determined several ways: using isotopic P analysis (Olsen and Watanabe, 1957; Holford and Patrick, 1979); calculating  $P_0$  from the linear sorption, which occurs at low P concentrations (Reddy et al., 1998; Pant and Reddy, 2001); applying extractable P concentrations (Sallade and Sims, 1997a; Siddique and Robinson, 2003); and most recently, by utilizing the analytical program Sigma Plot (Litaor et al., 2005).

The net equilibrium phosphorus concentration ( $EPC_0$ ) is defined as the phosphorus concentration where the amount of P sorption is equal to the amount of P desorption, resulting in a net P adsorption of zero (Figure 2.5). Graphically  $EPC_0$  is the point at which a particular phosphorus isotherm crosses the x-axis. The parameter is easily measured and permits an assessment as to whether sediment will release P or remove P from adjacent solution. If the  $EPC_0$  is greater than the P concentration in solution, the sediment will release P (House and Denison, 2002; Zhou et al., 2005). As such, the  $EPC_0$  is an important indicator of phosphorus concentrations available for plant uptake, or subject to runoff. Sallade and Sims (1997b) and Cooper and Gilliam (1987) suggested that the movement of P from drainage ditch sediments to floodwaters was dependent on the  $EPC_0$  and the soluble P concentration in chemically reduced sediments. Conversely, in a microcosm study, Young and Ross (2001) concluded that porewater phosphorus concentrations did not necessarily indicate the movement of P into floodwater, as high concentrations of P in porewaters did not move into adjacent

floodwater. Rather, these researchers hypothesized that redox chemistry affected the movement of P, thus the traditional calculation of  $EPC_0$  under oxidized conditions may not adequately describe the  $EPC_0$  of reduced wetland soils. These researchers recommended determining  $EPC_0$  values using anoxic soil overlain by oxidized floodwaters. Recent research has reported  $EPC_0$  levels, which were lower for aerobic peat layers than in anaerobic peat (Pant and Reddy, 2001; Litaor et al., 2005). Table 2.3 illustrates the various  $EPC_0$  values for different wetland soils/sediments, as published in the literature.

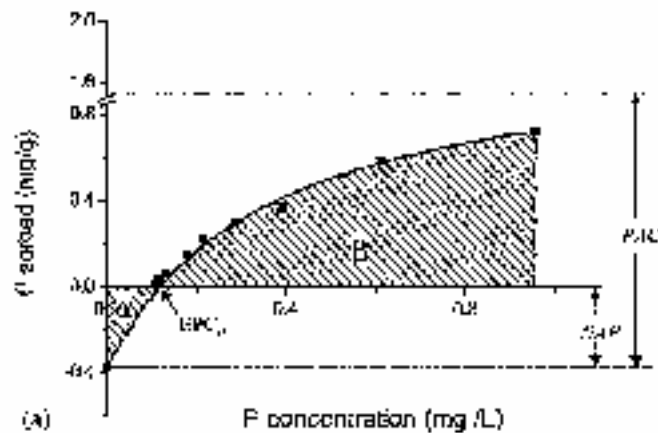


Figure 2.5. Sorption isotherm diagram to demonstrate the concepts of net phosphorus equilibrium concentration ( $EPC_0$ ), native adsorbed exchangeable phosphorus (NAP), and maximum phosphorus adsorption capacity (PAC) (Zhou et al., 2005).



Table 2.3. The mean total phosphorus  $EPC_0$  values of selected wetland soils/sediments.

| Soil/amendment type         | $EPC_0$ mg L <sup>-1</sup> | Study                  |
|-----------------------------|----------------------------|------------------------|
| Aerobic deep Histosols      | $0.03 \pm 0.01$            | Litaor et al., 2005    |
| Aerobic shallow Histosols   | $0.01 \pm 0.005$           | Litaor et al., 2005    |
| Anaerobic deep Histosols    | $0.11 \pm 0.05$            | Litaor et al., 2005    |
| Anaerobic shallow Histosols | $0.01 \pm 0.001$           | Litaor et al., 2005    |
| Drainage ditch              | 0.02 to 0.28               | Sallade and Sims, 1997 |
| Saprists                    | 0.13 to 0.30               | Young and Ross, 2001   |
| Aerobic lagoon sediments    | 0.01 to 0.19               | Pant and Reddy, 2001   |
| Anaerobic lagoon sediments  | 0.13 to 3.74               | Pant and Reddy, 2001   |

### Nitrogen & Wetlands

Unlike the phosphorus cycle, the nitrogen cycle contains a gaseous stage and may be viewed as a more complex, biologically mediated cycle (Richardson and Vepraskas, 2001). Nitrogen exists in wetlands systems in four predominant forms: ammonium ( $NH_4^+$ ), nitrate ( $NO_3^-$ ), dinitrogen gas ( $N_2$ ), and organic nitrogen. The amounts of ammonium, nitrate, and dinitrogen gas present in a wetland soil are dependent on microbial activity and water content (Figure 2.6). Denitrification rates within wetlands range from  $0.003$  to  $1.02$  g N m<sup>-2</sup> day<sup>-1</sup> (D'Angelo and Reddy, 1994). As a heterogeneous matrix, wetland soils contain oxygenated microsites allowing for aerobic nitrogen transformations. Nitrification (the conversion of  $NH_4^+$  to  $NO_3^-$  by bacteria) has been reported to occur at rates of  $0.01$  to  $0.16$  g N m<sup>-2</sup> day<sup>-1</sup> (D'Angelo and Reddy, 1994). Notably, it is the predominantly anaerobic conversion of soluble nitrate to nitrogen gas,  $N_2$ , (denitrification) and the slowed production of nitrate via nitrification that enables wetlands to reduce excessive and detrimental levels of nitrogen.

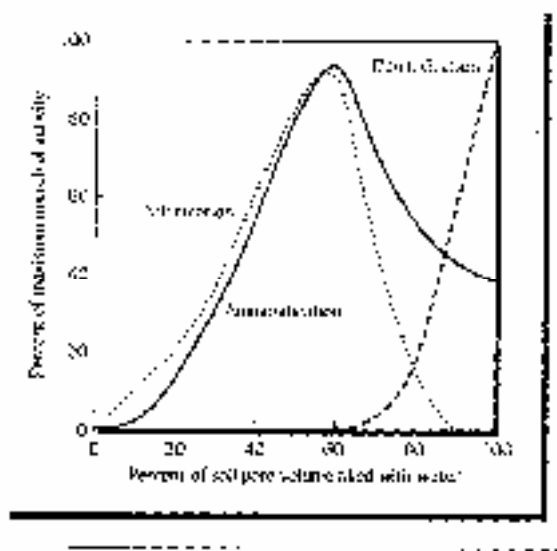


Figure 2.6. Rates of nitrification, ammonification and denitrification relative to the percentage of water-filled pore space (Brady and Weil, 1999).

Ammonification (the mineralization of organic-N into  $\text{NH}_4^+$ ) can take place under both aerobic and anaerobic conditions, although slower under the latter. Patrick (1982) reported a 7% loss of rye grass residues by weight in 84 days under anaerobic conditions as compared to a 17% loss in just 66 days under aerobic conditions. Although reduced, ammonification exceeds nitrification in wetland environments resulting in upwards of five times more  $\text{NH}_4^+\text{-N}$  than  $\text{NO}_3^-\text{-N}$  (Patrick, 1982).

### **Wetlands & Nutrient Removal**

From a water quality perspective, wetlands have been evaluated for their ability to remove nitrogen and phosphorus. Nitrogen is most efficiently removed by nitrification followed by denitrification. First nitrifying bacteria oxidize ammonium into nitrate, then in anoxic (anaerobic) zones, denitrifying bacteria convert nitrate to free gaseous nitrogen. Greater amounts of organic matter within the wetland increase the denitrification rate. Effective nitrate removal increases as organic matter ages and

accumulates (Spieles and Mitsch, 1998). In addition, lesser amounts of nitrogen can be removed through plant uptake in wetlands (Bavor et al., 1995). Phosphorus removal within wetlands is largely related to the reduction of sediment loads. As mentioned earlier, phosphorus is generally present in fixed forms due to adsorption, absorption, complexation and precipitation. Therefore, in retaining and reducing sediment loads, phosphorus levels decrease (Woltemade, 2000).

Woltemade (2000) reviewed the ability of restored wetlands to reduce both nitrogen and phosphorus concentrations in agricultural drainage water. The results of different case studies varied, but showed removal rates of up to 68% in nitrate and 43% for phosphorus. Woltemade asserts that there are two predominant governing factors in removal rates: the relative size of the wetland and drainage area, and the retention time. A minimum retention time of at least one to two weeks was recommended.

Kao and Wu (2001) studied the control of non-point source pollution from neighboring agricultural areas by a natural mountainous wetland in North Carolina. Their study demonstrated the removal of 86% ammonia, 80% nitrate, 91% suspended sediments and 59% total phosphorus. In reviewing wetland attributes governing the removal of non-point source pollution, the study identified the importance of the organic layer in water quality improvements (Kao and Wu, 2001).

Jordan et al. (2003) studied nutrient and sediment removal in a restored wetland. Although a reduction in nutrients was measured, removal percentages were less than observed by Kao and Wu (2001). After one year the wetland removed 59% of the total phosphorus and 38% of the total nitrogen from the influent. During a second year of

study, no significant removal of total nitrogen and phosphorus occurred. The lack of a drying period during the second year indicates that, in addition to wetland composition, size, and location, changes in hydrology affect non-point source pollution removal.

D'Angelo and Reddy (1994) studied nutrient removal in a restored peat marsh. In contrast to the previous studies discussed, nutrient levels increased. The initial flooding of fertilized organic agricultural soils resulted in increased concentrations of ammonia ( $\text{NH}_4^+$ ) and phosphorus (P). The study concluded that nutrient release was governed by four processes: 1) the initial flushing of nutrients; 2) the mineralization of organic matter; 3) anaerobiosis in the peat soil and floc sediment layers; and 4) transport mechanisms across the soil-water interface (Figure 2.7).

The recognition of the ability of natural wetland systems to prevent or reduce pollution has led to the study of constructed wetlands for such purposes as wastewater treatment and stormwater runoff mediation.

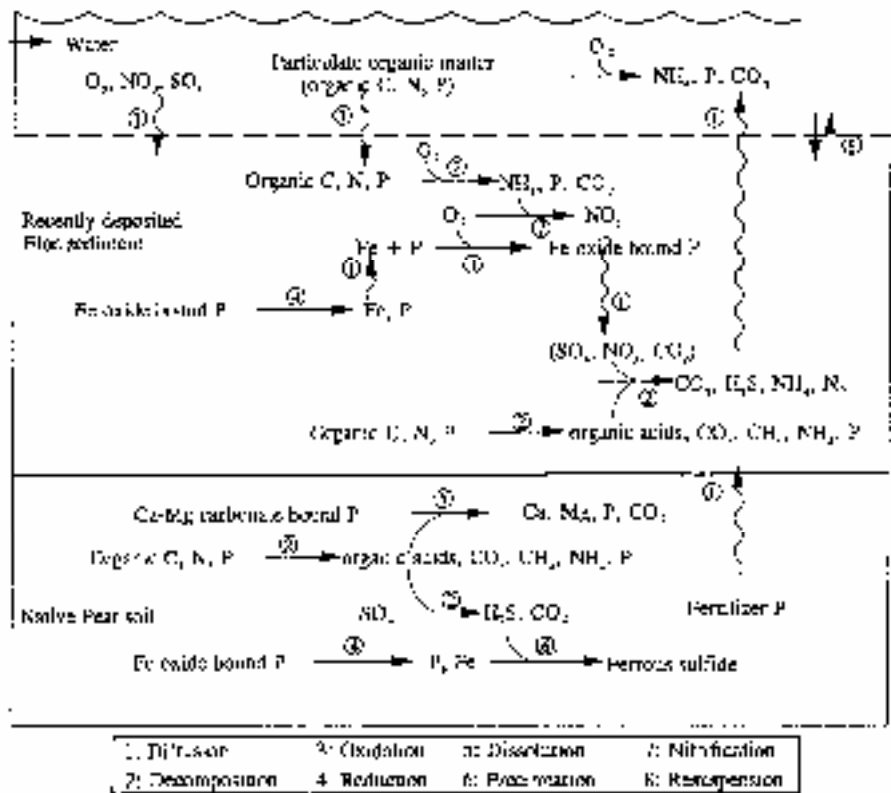


Figure 2.7. Conceptual diagram of mechanism which contribute to N and P release and exchange in the Lake Apopka constructed marsh (D'Angelo and Reddy, 1994).

## 2,4-D

Herbicides are a component of both agricultural and urban nonpoint source pollution. They are a principal tool in reducing economic losses caused by weeds, increasing yields and crop values. From a landscape and athletics perspective, herbicides are key in improving both aesthetic and wear quality in turf. Herbicides, however, may also contribute to environmental degradation via the contamination of ground and surface waters. The widely-used and controversial herbicide 2,4-dichlorophenoxy acetic acid (2,4-D), has been detected in aqueous environments (Goodrich et al., 1991; Gold et al., 1998; Rawn et al., 1999; IFEN, 2004) and linked to an

increased development of certain cancers in humans (Hoar et al., 1990; Hayes et al., 1995).

The leaching of herbicides into groundwater and runoff is dependent on physiochemical properties (Socias-Viciano et al., 1999). 2,4-D, a phenoxy herbicide used to control broadleaf weeds, has the following selected properties: molecular weight, 221.04;  $pK_a$  2.73; water solubility, 311 mg L<sup>-1</sup>;  $K_{ow}$ , 2.58 to 2.82; and half-life <7 days. According to the U.S. EPA (2005), agricultural uses of 2,4-D total 30 million pounds per year and non-agricultural uses total 16 million pounds per year. The herbicide 2,4-D has a low persistence in soil due to microbial degradation (half-life < 7 days), while in aerobic aquatic systems the half-life of 2,4-D ranges from 1 week to several weeks. Degradation of 2,4-D by microbes in aquatic environments is increased with increased sediment load, dissolved organic carbon and nutrients. Although 2,4-D has a relatively low persistence; the herbicide has been detected in both groundwater supplies and surface waters. 2,4-D is regulated under the Safe Drinking Water Act and has a maximum contamination level (MCL) of 0.07mg L<sup>-1</sup>.

### **2,4-D Sorption**

2,4-D sorption has been best described by the Freundlich isotherm (Boeston and van der Linden, 1991; Picton and Farenhorst, 2004; Farenhorst, 2006). The Freundlich isotherm is as follows:

$$S = K_F C^N$$

where  $S$  is the total sorbed 2,4-D ( $\mu\text{g g}^{-1}$ ), and  $C$  is the equilibrium concentration ( $\mu\text{g mL}^{-1}$ ),  $K_F$ , is the Freundlich sorption distribution coefficient [ $(\mu\text{g g}^{-1})/(\mu\text{g mL}^{-1})^N$ ], and  $N$  is a

dimensionless parameter indicating isotherm non-linearity. The sorption of hydrophobic organic compounds, like 2,4-D, by organic matter takes place via partitioning into flexible (expanded) and rigid (condensed) domains (Xing and Pignatello, 1997). The flexible domain creates a linear sorption isotherm whereas the rigid domain generates a nonlinear sorption isotherm (Gunasekara and Xing, 2003). The nonlinear sorption isotherm is ascribed to the aliphatic and aromatic moieties within both the flexible and rigid domains of organic matter (Xing 2001; Gunaskeras and Xing, 2003). Sorption distribution coefficients ranging from 0.81 to 2.89  $[(\mu\text{g g}^{-1})/(\mu\text{g mL}^{-1})^N]$  have been reported for mineral soils (varying organic matter contents) with initial 2,4-D concentrations from 1 to 16  $\mu\text{g mL}^{-1}$  (Picton and Farenhorst, 2004).

Past studies have demonstrated that factors influencing the sorption of 2,4-D include: organic matter content and quality, organic carbon content, clay type and content, pH, and ion exchange capacity (Benoit et al., 1996; Prado et al., 2001; Picton and Farenhorst, 2004). Benoit et al. (1996) reported increased sorption of 2, 4-D with the degree of organic matter humification: straw < lignin < composted straw < humic acid. Sorption was primarily driven by the dissociation of 2,4-D, which was complete in all suspensions, except for the humic acid suspension which had a comparatively low pH (3.3). Cox et al., (2000) attributed decreased sorption to the presence of highly humified organic matter and the repulsion between negatively charged 2,4-D molecules and carboxylic groups (an effect of both organic matter type and soil pH). The presence of aromatic structures in humic acids with a greater degree of maturity or altered lignin has been suggested to increase sorption via pi-pi bonding interactions (Dorado et al.,

2003). Recent studies, however, have demonstrated a strong affinity of hydrophobic organic compounds for aliphatic moieties (Chefetz et al., 2000; Li et al., 2003; Gunasekara and Xing, 2003). Piccolo et al. (1998) illustrated that the sorption of the moderately polar herbicide atrazine was better correlated with aliphatic humic acid than aromatic humic acid.

In addition to quality, the quantity of organic matter affects 2,4-D sorption. Increased levels of 2,4-D sorption have been reported in soil with high organic matter and organic carbon content as compared to soils with low organic matter/organic carbon content (Mcgrath, 1996; Wu et al., 2000; Prado et al., 2001; Dorado et al., 2003; Picton and Farenhorst, 2004). However, the extent of 2,4-D sorption increase attributed to organic matter is dependent on clay content, soil pH and organic matter quality (Benoit et al., 1996; Picton and Farenhorst, 2004). In addition to increasing sorption, high organic matter has also been attributed with decreasing 2,4-D desorption, indicating a strong affinity between 2,4-D and organic matter. (Bekbolet et al., 1999; Prado et al., 2001; Gaultier et al., 2006).

As a weakly acidic pesticide, the speciation of 2,4-D and subsequent sorption is pH dependent. 2,4-D undergoes greater sorption at low pH (< 2.8), where the herbicide is in molecular form (Weber, 1972). Spadotto and Hornsby (2003) measured 2,4-D sorption under varying pH and observed a significant drop in sorption at higher pH, where 2,4-D is mainly present in anionic form. The sorption coefficients for 2,4-D sorption were greatest at pH 2.5 and decreased with increasing pH, with the lowest coefficients at 6.2 (Spadotto and Hornsby, 2003). Similarly, maximum 2,4-D sorption has



been reported at pH 4 (Alam et al., 2002) and weak sorption by soils with mean pH values of 7.2 and 7.4 (Farenhorst et al., 2001). In addition to affecting the degree of ionization of the herbicide, pH influences the charge density of organic matter which then further affects sorption dynamics. The effect is reportedly more pronounced when the pKa of the weakly acidic herbicide is within about 2 units of the soil pH (Ahrens, 1994; Farenhorst et al., 2001; Gaultier et al., 2006).

Other less predominant factors affecting 2,4-D sorption include: increased sorption with high amorphous iron and aluminum oxide content (Rodriguez-Rubio et al., 2006), increased sorption with lower landscape position (Farenhorst et al., 2001), and decreased sorption with increasing soil carbonate content (Gaultier et al., 2006).

## CHAPTER 3

### CHEMICAL AND PHYSICAL CHARACTERIZATION OF TWO COMMERCIALY AVAILABLE COMPOSTS AND TWO ORGANIC WETLAND SOILS

#### Introduction

The organic matter within natural freshwater wetlands has a primary role in supplying wetland plant nutrients, providing a carbon source for microbial populations and in retaining nonpoint source pollutants. These functions are dependent on several physio-chemical properties. Predominant governing properties include: nutrient content, percent organic matter, pH, redox status, and elemental composition. Understanding the physio-chemical properties of natural wetlands soils aids in the determination of appropriate soil amendment use in mitigation wetlands. This means that before the natural wetland soil environment can be mimicked, an inventory and understanding of the characteristics inherent to this environment must be ascertained. The tremendous variation among wetland systems and wetland soils makes this a formidable task. Nevertheless, an arbitrary use of organic amendments in the construction of mitigation wetlands may result in the failure of mitigation wetlands to replace the functions of lost or damaged wetlands.

#### Materials

Two commercially available composts were evaluated: Quoddy Blend Lobster Compost and Agresoil Leaf Compost. The Quoddy Blend Lobster Compost is produced in New Brunswick Canada for the Coast of Maine Company. The lobster compost is fully matured and made entirely from crab, salmon and lobster waste, aspen bark, and

composted cow manure. The Agresource Company produces Agresoil Leaf Compost throughout the state of Massachusetts. The Agresoil Leaf Compost is created from leaves and yard wastes. Agresoil Leaf Compost has been used in wetland replication and restoration projects throughout New England. Two different naturally occurring organic wetland soils were also evaluated. A peat soil was collected from an acidic bog dominated by black spruce (*Picea mariana*) and moss (*Spagnum spp.*) located in Plainfield, MA. A muck soil was collected from a sensitive fern (*Onoclea sensibilis*) and sedge (*Carex spp.*) dominated wetland located in Pittsfield, MA. The muck and peat soils were collected from undisturbed areas situated at least 3.5 meters from the wetland boundary. Sample spots were identified, the vegetative cover was carefully removed and the uppermost 16-inches of organic matter were collected. Subsamples were then combined and mixed to create a composite sample. All organic materials were air-dried, homogenized by hand, passed through a 2-mm sieve, and homogenized by hand a second time. Samples were stored in air-tight containers at 4°C.

### **Methods**

A Jarrel-Ash Model 955 ICP-AES was used to analyze total nutrients. Prior to analysis, samples were prepared by dry ashing following methodology as presented by Greweling (1976). Extractable nutrients were determined using Morgan's extracting solution and following methodology as presented by the Soil and Plant Analysis Council, Inc. (1992). pH was determined using a 1:7 organic matter to water ratio, to ensure an adequate amount of solution to attain an accurate measurement. Organic material pH was measured using a glass electrode-calomel electrode pH meter (Fisher

Accumet model #805). Percent organic matter was determined by loss on ignition (Soil and Plant Analysis Council, Inc., 1992). Particle size analysis was performed on the compost samples (Gee and Bauder, 1986). Nitrogen, carbon and hydrogen content were determined using a 240XA Elemental Analyzer (Shelton, CT). Ash content was determined by heating the samples to 740°C for 4 hours (Xing, 2001). The oxygen content was then calculated by the mass difference.

Recent studies have reported a strong correlation between phosphorus sorption and oxalate-extractable iron and aluminum (Reddy et al., 1998; Dunne et al., 2005; Litaor et al., 2005; Yoo et al., 2006). To study this relationship oxalate-extractable iron, aluminum, manganese, and phosphorus levels of the four different organic materials were determined (Loeppert and Inskeep, 1996).

All extractions were performed in triplicate. Data were subjected to a standard analysis of variance (ANOVA) followed by mean separation if the ANOVA f test indicated significant differences among treatment means using the SAS System, Version 9.1.3 (SAS Institute, Inc., 2004).

### **Spectroscopic Characterization**

Solid-state carbon-13 Nuclear Magnetic Resonance (CP-MAS  $^{13}\text{C}$  NMR) spectra were obtained with a Bruker DSX-300 spectrometer (Karlsruhe, Germany) operated at the  $^{13}\text{C}$  frequency of 75MHz. The spectra were divided into specific chemical shift regions, as follows: paraffinnic carbons (0-50 ppm), alcohols, carbohydrates, ethers, amines, methoxyl and acetyl carbons (50-109 ppm), aromatic and phenolic carbons (109-163 ppm), carboxyl carbons (163-190 ppm), and carbonyl carbons (190-220 ppm) (Kang

et al., 2003). The aliphatic carbon and aromatic carbon were determined based on the 0-109 ppm region and 109-163 ppm region, respectively. The total aliphatic and aromatic carbon contents were expressed as percentage of the whole (aromatic plus aliphatic). Important functional groups were identified by Attenuated Total Reflectance Fourier Transformed Infrared (ATR-FTIR) spectroscopy using a Perkin-Elmer Spectrum (Wellesley, MA). The ATR-FTIR spectra between 650 and 4000  $\text{cm}^{-1}$  were obtained for the four organic materials. Due to the high mineral content of the composts and the need to remove iron for NMR analyses, subsamples were passed through a 500-  $\mu\text{m}$  sieve and subject to a HF pretreatment prior to both NMR and FTIR analysis (Preston and Newman, 1995). Despite possible losses of C and N via the HF treatment process, no major differences in organic matter composition have been reported (Dalmolin et al., 2005; Gonçalves et al., 2003).

The majority of the characterizations were performed in triplicate with the exception of the elemental analysis, which was performed in duplicate. Data were subjected to a standard analysis of variance (ANOVA), followed by mean separation if the ANOVA f test indicated significant differences among treatment means using the SAS System, Version 9.1.3 (SAS Institute, Inc., 2004)

## **Results & Discussion**

### **pH**

The four organic materials displayed marked variation among the selected physio-chemical properties. Both composts demonstrated significantly higher pH values as compared to the natural wetland soils, 7.70, 7.56, 5.95, and 3.87 for leaf compost, lobster

compost, muck, and peat, respectively (Table 3.1). Natural wetland systems exhibit a wide range in pH. The classification of wetlands by U.S. Fish and Wildlife Service distinguishes three pH modifiers: acid wetlands have a pH less than 5.5, circumneutral wetlands have a pH ranging from 5.5 to 7.4, and alkaline wetlands have a pH greater than 7.4. Mineral wetland soils tend to have a circumneutral pH while organic wetland soils are generally acidic (Mitsch and Gosselink, 2000). The low pH measured for the peat material is typical of sphagnum moss and black spruce dominated wetlands. Likewise, the circumneutral pH of the muck soil is representative of the majority of freshwater wetland systems. The alkaline condition of the two composts is likely due to the addition of lime during the composting processes. In addition, the lobster and crab shells within the lobster compost may be adding significant amounts of  $\text{CaCO}_3$ . Although the specific composting processes were not disclosed by the manufactures, the addition of lime is a common composting practice that would result in an increase in alkalinity.

Table 3.1. Selected physio-chemical properties of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Selected Physio-chemical Properties |        |      |                 |                 |                 |
|----------------------|-------------------------------------|--------|------|-----------------|-----------------|-----------------|
|                      | pH                                  | %OM    | C/N  | %sand           | %silt           | %clay           |
| Lobster <sup>†</sup> | 7.56 b                              | 25.9 d | 27.3 | 81.0            | 18.8            | 0.2             |
| Leaf <sup>†</sup>    | 7.70 a                              | 28.5 c | 14.5 | 77.7            | 21.0            | 1.4             |
| Muck <sup>‡</sup>    | 5.95 c                              | 76.2 b | 20.1 | ND <sup>a</sup> | ND <sup>a</sup> | ND <sup>a</sup> |
| Peat <sup>‡</sup>    | 3.87 d                              | 93.1 a | 29.8 | ND <sup>a</sup> | ND <sup>a</sup> | ND <sup>a</sup> |
|                      | **                                  | **     |      |                 |                 |                 |

\*\* Significant at the 0.01 probability level

<sup>a</sup> ND: not determined

### **Percent Organic Matter**

Both composts had lower organic matter content than the natural wetland soils (Table 3.1). Due to the comparatively low amount of organic matter present in the compost samples, particle size analysis was performed to determine the mineral composition of the composts. Both composts had high percentages of sand; 55.5% and 60.3% for the leaf and lobster composts, respectively. The high mineral component of the composts brings rise to a potential regulatory issue. Current mitigation guidelines within the state of Massachusetts recommend the addition of organic material to produce an A-horizon comprised of equal volumes of organic and mineral materials (MA DEP, 2002). The addition of compost containing a substantial mineral component may result in an inadvertent increase in the mineral to organic ratio of the created A-horizon. The higher percentage of organic matter in wetland soils is an important distinction between wetland and upland soils. In addition, the percentage of organic matter within a wetland soil is a predominant governing factor in the reduction of a majority of pollutants whether directly (organo-complexations) or indirectly (microbial population, water retention, redox, and pH). The assumption that these organic amendments are entirely or prominently comprised of organic materials may be erroneous.

### **Total Nutrient Content**

The total and available nutrient content of wetland soils varies greatly with wetland type and is dependent on factors such as soil parent material, organic matter content, pH, landscape position and hydrology. Inland freshwater wetlands that are

“open” tend to have high nutrient contents due to the exchange with adjacent ecosystems via runoff, flooding and groundwater. Conversely, “closed” inland freshwater systems that are isolated within the landscape (ombrotrophic bogs) are typically nutrient poor. The nutrient input of a closed wetland system is primarily depended on direct precipitation and dry deposition.

The total nutrient levels of the four organic materials varied. As illustrated in Table 3.2., the composts had significantly higher levels of total phosphorus (P) and potassium (K). Total P levels of organic wetland soils have been reported to range from 3.0 to 1,300 mg kg<sup>-1</sup> (Johnston, 1991). While the total P levels of the two wetland soils fall within the reported range, both composts demonstrated higher total P levels higher than the reported range. Total K levels are not typically reported for wetland soils. As such, a comparison with published literature was not possible. However, the higher amounts of total K exhibited by the composts (greater than six times the total K observed in the soil samples) demonstrates the nutrient differences between the organic materials within this study.

Levels of calcium and magnesium observed for the compost samples and muck soils are attributed to the use of lime during the composting process and the limestone parent material of the muck soil sample. These levels are higher than those reported for non-calcareous wetland soils. Corstanje et al. (2006) reported total calcium levels of 15,971 and 17,354 mg kg<sup>-1</sup> and total magnesium levels of 1,928 and 1,993 mg kg<sup>-1</sup> for a Northern Everglade marsh. The high total iron content (Table 3.3) of the compost samples as compared to the soil samples is ascribed to the higher mineral content as



previously discussed. Zhang et al. (2004) reported comparable findings: a total iron content of 16,100 mg kg<sup>-1</sup> for a sewage sludge/yard waste compost and a total iron content of 3,730 mg kg<sup>-1</sup> for a peat.

Table 3.2. Mean total macronutrient levels of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Mean Total Macronutrients* |             |               |             |
|----------------------|----------------------------|-------------|---------------|-------------|
|                      | P                          | K           | Ca            | Mg          |
|                      | mg kg <sup>-1</sup>        |             |               |             |
| Lobster <sup>†</sup> | 2454 ± 34 a                | 3513 ± 22 b | 30770 ± 370 b | 4672 ± 24 a |
| Leaf <sup>†</sup>    | 2410 ± 56 a                | 3838 ± 45 a | 14057 ± 212 c | 3485 ± 42 b |
| Muck <sup>‡</sup>    | 1279 ± 33 b                | 529 ± 10 c  | 32807 ± 586 a | 4686 ± 77 a |
| Peat <sup>‡</sup>    | 1333 ± 15 c                | 382 ± 29 d  | 1353 ± 18 d   | 329 ± 7 c   |
|                      | **                         | **          | **            | **          |

\* Means within a column followed by the same letter are not significantly different according to Duncan's New Multiple Range Test.

\*\* Significant at the 0.01 probability level

Table 3.3. Mean total micronutrient levels of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Mean Total Micronutrients* |                 |                |               |               |
|----------------------|----------------------------|-----------------|----------------|---------------|---------------|
|                      | B                          | Mn              | Zn             | Cu            | Fe            |
|                      | mg kg <sup>-1</sup>        |                 |                |               |               |
| Lobster <sup>†</sup> | 26.2 ± 0.8 b               | 1110.0 ± 12.1 a | 168.0 ± 5.3 b  | 53.0 ± 2.4 c  | 13440 ± 141 a |
| Leaf <sup>†</sup>    | 36.2 ± 1.4 a               | 301.1 ± 3.2 c   | 265.4 ± 50.9 a | 148.7 ± 4.0 a | 10320 ± 221 b |
| Muck <sup>‡</sup>    | 17.2 ± 0.8 c               | 667.5 ± 11.8 b  | 118.0 ± 5.1 c  | 39.7 ± 3.6 d  | 9722 ± 272 c  |
| Peat <sup>‡</sup>    | 2.2 ± 0.0 d                | 33.3 ± 0.1 d    | 77.6 ± 10.0 c  | 59.4 ± 1.6 b  | 1081 ± 14 d   |
|                      | **                         | **              | **             | **            | **            |

\* Means within a column followed by the same letter are not significantly different according to Duncan's New Multiple Range Test.

\*\* Significant at the 0.01 probability level.

High levels of total manganese for the lobster compost may be attributed to high manganese concentrations present in lobster shells due to bioaccumulation (Baden and Neil, 2003). Bjerredaard and Depledge (2002) reported that crab exoskeletons contained 95% of the total body content of manganese. In a study of manganese solubilization in soils affected by acid mine runoff, Green et al. (2003) reported total manganese levels lower than that of the lobster compost (729 to 868 mg kg<sup>-1</sup>). Notably, the chemical reduction of manganese within an anaerobic wetland environment may result in toxic levels of plant available manganese (Smith, 1990). Both compost samples had higher levels of total Ni and Cr as compared with the soil samples, and the leaf compost had the highest total Pb content (Table 3.4). The total Cd levels of the compost were comparable to those reported for sewage sludge/yard waste compost. Nickel and aluminum levels however, were much higher for the composts evaluated in this study as compared to those reported for a sewage sludge/yard waste compost (1.1 mg kg<sup>-1</sup> and 4,850 mg kg<sup>-1</sup>, respectively) (Zhang et al., 2004). Total nickel levels of the compost were more closely aligned with those of soils affected by acid mine runoff (12.8 to 14.3 mg kg<sup>-1</sup>) (Green et al., 2003).

#### **Extractable Nutrient Content**

Morgan's extracting solution was used to determine the nutrient content readily available for plant uptake. The composts had significantly higher levels of extractable phosphorus and potassium (Table 3.5), which concurs with the reported total nutrient levels. Extractable K levels of freshwater wetland soils have been reported to range from 87 to 319 mg kg<sup>-1</sup> (Young and Ross, 2001). Both composts samples exhibited

extractable K levels at least 2 times greater than the previously reported range (Young and Ross, 2001) and more than 5 times the extractable K levels of the soils examined for this study. Although K toxicity is generally not an issue in plants, the higher total K levels present in the compost samples is a further illustration of the chemical nutrient differences as compared to wetland soils.

Table 3.4. Mean total metal levels of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Mean Total Metals*  |               |             |              |              |
|----------------------|---------------------|---------------|-------------|--------------|--------------|
|                      | Pb                  | Al            | Cd          | Ni           | Cr           |
|                      | mg kg <sup>-1</sup> |               |             |              |              |
| Lobster <sup>†</sup> | 4.7 ± 0.1 c         | 15333 ± 148 a | 2.5 ± 0.1 a | 19.1 ± 0.4 a | 20.4 ± 0.9 a |
| Leaf <sup>†</sup>    | 13.0 ± 0.2 a        | 9157 ± 114 b  | 1.8 ± 0.0 b | 15.1 ± 0.8 b | 17.9 ± 0.8 b |
| Muck <sup>‡</sup>    | 4.4 ± 0.2 c         | 7612 ± 207 c  | 2.5 ± 0.1 a | 9.0 ± 0.3 c  | 7.8 ± 0.3 c  |
| Peat <sup>‡</sup>    | 9.1 ± 0.1 b         | 9149 ± 57 b   | 0.8 ± 0.1 c | 7.2 ± 0.8 d  | 1.8 ± 0.1 d  |
|                      | **                  | **            | **          | **           | **           |

\* Means within a column followed by the same letter are not significantly different according to Duncan's New Multiple Range Test.

\*\* Significant at the 0.01 probability level.

Table 3.5. Mean Morgan's extractable macronutrient levels of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Mean Morgan's Extractable Macronutrients* |                 |                  |                 |
|----------------------|---|-----------------|------------------|-----------------|
|                      | P   | K               | Ca               | Mg              |
|                      | mg kg <sup>-1</sup>                       |                 |                  |                 |
| Lobster <sup>†</sup> | 90.0 ± 2.3 b                              | 653.9 ± 6.6 b   | 8458.0 ± 128.4 a | 482.8 ± 13.0 c  |
| Leaf <sup>†</sup>    | 130.6 ± 2.4 a                             | 1426.5 ± 26.9 a | 3445.5 ± 54.7 b  | 547.1 ± 11.0 b  |
| Muck <sup>‡</sup>    | 13.7 ± 1.1 c                              | 26.5 ± 1.7 d    | 5780.7 ± 181.4 c | 1213.0 ± 37.2 a |
| Peat <sup>‡</sup>    | 20.0 ± 5.4 c                              | 122.9 ± 61.6 c  | 559.5 ± 99.9 d   | 100.7 ± 28.3 d  |
|                      | **  | **              | **               | **              |

\* Means within a column followed by the same letter are not significantly different according to Duncan's New Multiple Range Test.

\*\* Significant at the 0.01 probability level

Extractable boron and manganese levels in the composts were significantly higher than the wetland soils (Table 3.6.). The presence of high amount of extractable manganese, as well as high total manganese, reinforces the presumption that manganese levels released into a newly constructed mitigation wetland (particularly from the lobster compost) may be detrimental to plant growth. Some wetland plant species have demonstrated physiological adaptations, which result in high manganese tolerance (Ernst, 1990). However, studies have documented that manganese tolerance varies greatly with plant species (Fageria, 2001; Beaton and Dudley, 2004). Such variations may occur among wetland as well as upland plant species. The extractable manganese level of the lobster compost was lower than those reported by Ahn and Mitsch (2001) for 2-year-old wetland soil mesocosms lined with coal combustion products (102 to 128 mg kg<sup>-1</sup>). However, the extractable manganese levels observed for the lobster compost do not reflect additional manganese release under anaerobic conditions.

Although the composts had higher total iron contents, the peat soil and lobster compost had the highest levels of extractable iron, 12.8 and 11.1 mg kg<sup>-1</sup>, respectively, thus indicating that the iron present in the leaf compost is held in a more stable form as compared to the lobster compost and peat soil. However, the release of iron by the leaf compost may increase under anaerobic conditions as ferric iron is reduced to ferrous iron. The extractable aluminum concentration was greatest for the peat soil as compared to all other samples. The extractable aluminum levels of peat soil reflects the acidic bog system where the peat soil was collected (Table 3.7). The sphagnum moss and black spruce dominating the acidic bog have adapted to tolerate high levels of aluminum,

whereas other upland and wetland plant species may suffer from aluminum toxicity if exposed to similar concentrations (Ruttner, 1963; Malmer, 1975).

Table 3.6. Mean Morgan's extractable micronutrient levels of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Mean Morgan's Extractable Micronutrients* |              |              |           |              |
|----------------------|---|--------------|--------------|-----------|--------------|
|                      | B   | Mn           | Zn           | Cu        | Fe           |
|                      | mg kg <sup>-1</sup>                       |              |              |           |              |
| Lobster <sup>†</sup> | 1.9 ± 0.0 b                               | 71.0 ± 1.1 a | 13.0 ± 0.1 a | 1.1 ± 0.1 | 11.1 ± 0.1 b |
| Leaf <sup>†</sup>    | 3.2 ± 0.1 a                               | 20.3 ± 0.2 b | 4.5 ± 0.2 c  | 0.9 ± 0.1 | 6.9 ± 0.1 c  |
| Muck <sup>‡</sup>    | 0.5 ± 0.0 c                               | 11.8 ± 0.7 c | 4.5 ± 0.7 c  | 1.0 ± 0.2 | 6.2 ± 0.3 c  |
| Peat <sup>‡</sup>    | 0.3 ± 0.1 d                               | 8.4 ± 0.2 d  | 10.1 ± 0.3 b | 1.0 ± 0.6 | 12.8 ± 0.9 a |
|                      | **  | **           | **           | ns        | **           |

\* Means within a column followed by the same letter are not significantly different according to Duncan's New Multiple Range Test.

\*\* Significant at the 0.01 probability level

Table 3.7. Mean Morgan's extractable metal levels of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Mean Morgan's Extractable Metals* |                |               |              |               |
|----------------------|-----------------------------------|----------------|---------------|--------------|---------------|
|                      | Pb                                | Al             | Cd            | Ni           | Cr            |
|                      | mg kg <sup>-1</sup>               |                |               |              |               |
| Lobster <sup>†</sup> | 1.0 ± 0.5 c                       | 14.2 ± 1.0 b   | 0.24 ± 0.0 ab | 0.15 ± 0.0 b | 0.13 ± 0.0 b  |
| Leaf <sup>†</sup>    | 2.2 ± 0.3 b                       | 11.8 ± 0.3 b   | 0.15 ± 0.0 b  | 0.10 ± 0.0 b | 0.10 ± 0.0 bc |
| Muck <sup>‡</sup>    | 1.8 ± 0.1 bc                      | 12.5 ± 1.8 b   | 0.28 ± 0.0 a  | 0.12 ± 0.0 b | 0.18 ± 0.0 a  |
| Peat <sup>‡</sup>    | 10.5 ± 0.9 a                      | 504.5 ± 10.9 a | 0.16 ± 0.1 b  | 0.43 ± 0.0 a | 0.06 ± 0.0 c  |
|                      | **                                | **             | **            | **           | **            |

\* Means within a column followed by the same letter are not significantly different according to Duncan's New Multiple Range Test.

\*\* Significant at the 0.01 probability level

### Oxalate Extraction

Recent studies on constructed wetlands (Dunne et al., 2005; Yoo et al., 2006), altered wetlands (Litaor et al., 2005), and natural wetlands (Reddy et al., 1998) have demonstrated a strong correlation between oxalate-extractable aluminum and iron levels and phosphorus sorption by soils/sediments. As illustrated in Table 3.8, the composts

had significantly different levels of oxalate extractable iron, aluminum, and phosphorus as compared with the wetland soils. These differences may indicate mechanisms involved in the sorption of phosphorus by the four organic materials. An evaluation of the relationship between the oxalate extraction and phosphorus sorption results is presented in Chapter 5.

Table 3.8. The mean oxalate-extractable iron, aluminum, manganese, and phosphorus concentrations of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Mean Oxalate Extractable* |              |            |             |
|----------------------|---------------------------|--------------|------------|-------------|
|                      | Fe                        | Al           | Mn         | P           |
|                      | mg kg <sup>-1</sup>       |              |            |             |
| Lobster <sup>†</sup> | 1876 ± 143 b              | 1754 ± 109 b | 193 ± 20 a | 775 ± 53 a  |
| Leaf <sup>†</sup>    | 1558 ± 222 c              | 1723 ± 189 b | 42 ± 5 c   | 786 ± 103 a |
| Muck <sup>‡</sup>    | 2609 ± 87 a               | 2134 ± 66 a  | 217 ± 7 a  | 215 ± 8 b   |
| Peat <sup>‡</sup>    | 623 ± 47 d                | 637 ± 17 c   | 140 ± 17 b | 62 ± 11 b   |
|                      | **                        | **           | **         | **          |

\*Means within a column followed by the same letter are not significantly different according to Duncan's New Multiple Range Test.

\*\* Significant at the 0.01 probability level

### Elemental Analyses

Elemental analysis and atomic ratio data were obtained using 2-mm and 500-µm size fractions (Table 3.9 and Table 3.10). The 2-mm size fraction was chosen to represent the fine-earth soil fraction of the samples (i.e. sample without coarse fragments such as twigs, gravel, large plant residues). The 500-µm size fraction was selected for analysis based on the previously described HF pretreatment prior to NMR analysis (which resulted in materials of this grain size).

A comparison between the elemental analyses of the two size fractions indicates little compositional change between the 500-µm and 2-mm size fractions (Tables 3.9 and

3.10). The 500- $\mu\text{m}$  size fraction of the peat soil had the highest organic carbon content (42.74%). The 500- $\mu\text{m}$  size fraction of the lobster compost had the lowest carbon content (15.35%). In general, both wetland soils had higher organic carbon content as compared to the compost samples. This is consistent with the higher mineral content of the composts previously reported. H/C atomic ratio denotes the aliphaticity of the organic materials. All samples and size fractions had relatively high H/C ratios, indicating a predominance of aliphatic C. The polarity, as determined by the (O+N)/C atomic ratio, ranged from 0.41 to 0.81 in all samples. Within both size fractions, the polarity was highest in the wetland soils. Polar compounds within the molecular structure of plant cells include: polysaccharides, carbohydrates, glucose, phospholipids, and phenolics such as flavonoids, tannins, lignins, and salicylic acid (Raven et al., 1999). During the decomposition process of organic materials, the labile materials (such as sugars, starches and simple proteins) are readily transformed, resulting in comparatively higher amounts of more resistant components such as cellulose, fats, waxes, lignins and phenolic compounds (Brady and Weil, 2002). The higher polarity of the wetland soils may be attributed to the decreased rate of decomposition within an anaerobic wetland environment as compared to the aerated decomposition during composting processes.

Table 3.9. Mean elemental analysis and atomic ratios of 500-micron size fraction of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Elemental Analysis |       |      |      |       |      |       |
|----------------------|--------------------|-------|------|------|-------|------|-------|
|                      | % ASH              | %C    | %N   | %H   | %O    | H/C  | O+N/C |
| Lobster <sup>†</sup> | 70.79              | 15.35 | 0.61 | 2.10 | 11.15 | 1.63 | 0.58  |
| Leaf <sup>†</sup>    | 68.43              | 17.06 | 1.36 | 2.15 | 11.00 | 1.50 | 0.55  |
| Muck <sup>‡</sup>    | 17.79              | 37.34 | 1.86 | 4.81 | 38.20 | 1.53 | 0.81  |
| Peat <sup>‡</sup>    | 14.11              | 42.74 | 2.37 | 5.39 | 35.40 | 1.67 | 0.75  |

Table 3.10. Mean elemental analysis and atomic ratios of 2-mm size fraction of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Elemental Analysis |       |      |      |       |      |       |
|----------------------|--------------------|-------|------|------|-------|------|-------|
|                      | % ASH              | %C    | %N   | %H   | %O    | H/C  | O+N/C |
| Lobster <sup>†</sup> | 66.48              | 17.93 | 0.66 | 2.40 | 12.54 | 1.59 | 0.56  |
| Leaf <sup>†</sup>    | 67.94              | 19.25 | 1.33 | 2.47 | 9.00  | 1.53 | 0.41  |
| Muck <sup>‡</sup>    | 24.28              | 38.04 | 1.90 | 4.78 | 31.00 | 1.50 | 0.65  |
| Peat <sup>‡</sup>    | 6.97               | 42.56 | 1.50 | 6.13 | 40.81 | 1.65 | 0.72  |

### ATR-FTIR Characterization

Figure 3.1. illustrates the ATR-FTIR spectra obtained for the four organic materials. All samples exhibited bands at 1030, 1635, and 1731  $\text{cm}^{-1}$ , associated with the C-O stretching in polysaccharides, the asymmetric C-O-C stretching vibration, and the potentially hydrogen-bonded, carbon-oxygen stretching vibration of the carbonyl bond within ester groups, respectively. The wetland soils displayed stronger bands at 1030  $\text{cm}^{-1}$  which corresponds with their reported higher polarity. Likewise the wetland soils had more pronounced bands at 1163 and 1731  $\text{cm}^{-1}$ , which have been associated with the cutin component of organic matter (Chen et al., 2005). Cutin is the high molecular weight structural component of plant cuticle which reportedly persists during decomposition (Nierop, 1998; Almendros et al., 2000). The diminished bands exhibited



in the compost spectra at 1163 and 1731  $\text{cm}^{-1}$  may be due to the overall lower carbon content as opposed to being indicative of a lesser degree of decomposition.

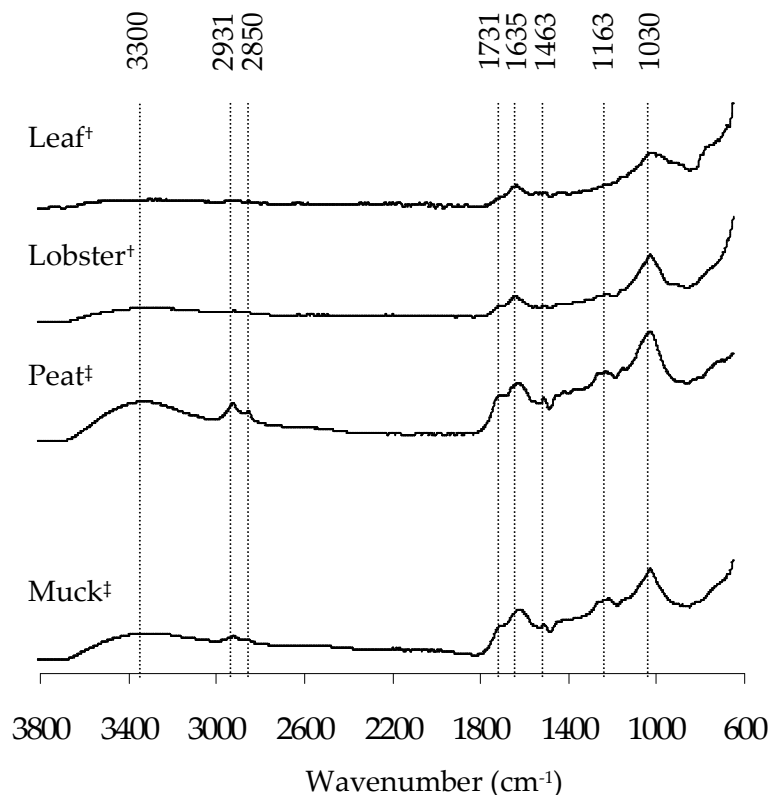


Figure 3.1. The ATR-FTIR spectra of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

All four spectra displayed bands at 1635  $\text{cm}^{-1}$  denoting the phenolic compounds. Defined bands at 1463, 2850, 2931, and 3300  $\text{cm}^{-1}$  were present in the wetland soil samples, but were absent in the compost spectra. The 1463  $\text{cm}^{-1}$  peak has been assigned to the methyl group bending vibration (Chamel and Marechal, 1992). Peaks at 1463 and 1635  $\text{cm}^{-1}$  depict the aromatic domain of the organic materials comprised of phenolic compounds such as tannins and lignins. The bands located at 2850 and 2931  $\text{cm}^{-1}$  are associated with the symmetric and asymmetric stretching vibration of methylene

groups, respectively, and denote the aliphatic region of the spectra. Bands located at  $2931\text{ cm}^{-1}$  have been highly associated with the aliphatic portion of cutin (Chefetz, 2003; Chen et al., 2005). The dominant band is present in the peat soil spectrum which concurs with the high percent aliphatic carbon determined by elemental analysis. The broad band located at  $\sim 3300\text{ cm}^{-1}$  denotes the stretching vibration of H-bonded hydroxyl functional groups and is distinct for the two wetland soils.

### **$^{13}\text{C}$ NMR Characterization**

The solid-state  $^{13}\text{C}$  NMR spectra for the four organic materials are illustrated in Figure 3.2. Distinct peaks at 29 ppm and 32 ppm were present in all spectra except the lobster compost, which exhibited a diminished peak. These peaks represent the aliphatic paraffinic region. The percent paraffinic C for the organic materials ranged from 17% to 24%; the lobster compost having the lowest percentage (Table 3.11). The leaf compost and muck soil exhibited strong peaks at 55 ppm (methoxyl C). All organic materials had dominant peaks at 72 ppm (O-alkyl carbon in carbohydrates), 105 ppm (anomeric carbon of polysaccharides), and 172 ppm (carboxyl/amide carbons). The absence of a strong peak at 130 ppm (C-substitutes aromatic carbons) for all spectra indicates low aromatic carbon content. This is confirmed by the integration data (Table 3.10), which depicts percent aromatic C ranging from 20% to 33%. These percentages are relatively low as compared to the percent aliphatic C which ranged from 67% to 80%. The relatively high percentages of aliphatic C concur with the H/C ratios determined via elemental analysis (Table 3.9 and Table 3.10). The combination of defined peaks near 150 ppm and 55 ppm is attributed to phenolic C. This combination was present for the

lobster compost, leaf compost, and muck soil, but not the peat soil. As such, the polarity of the peat soil is most likely attributed to the high polysaccharide content rather than phenolic compounds such as tannins and lignins. Notably the presence of phenols within the composts was visually confirmed by the high tannin coloration of the compost filtrates.

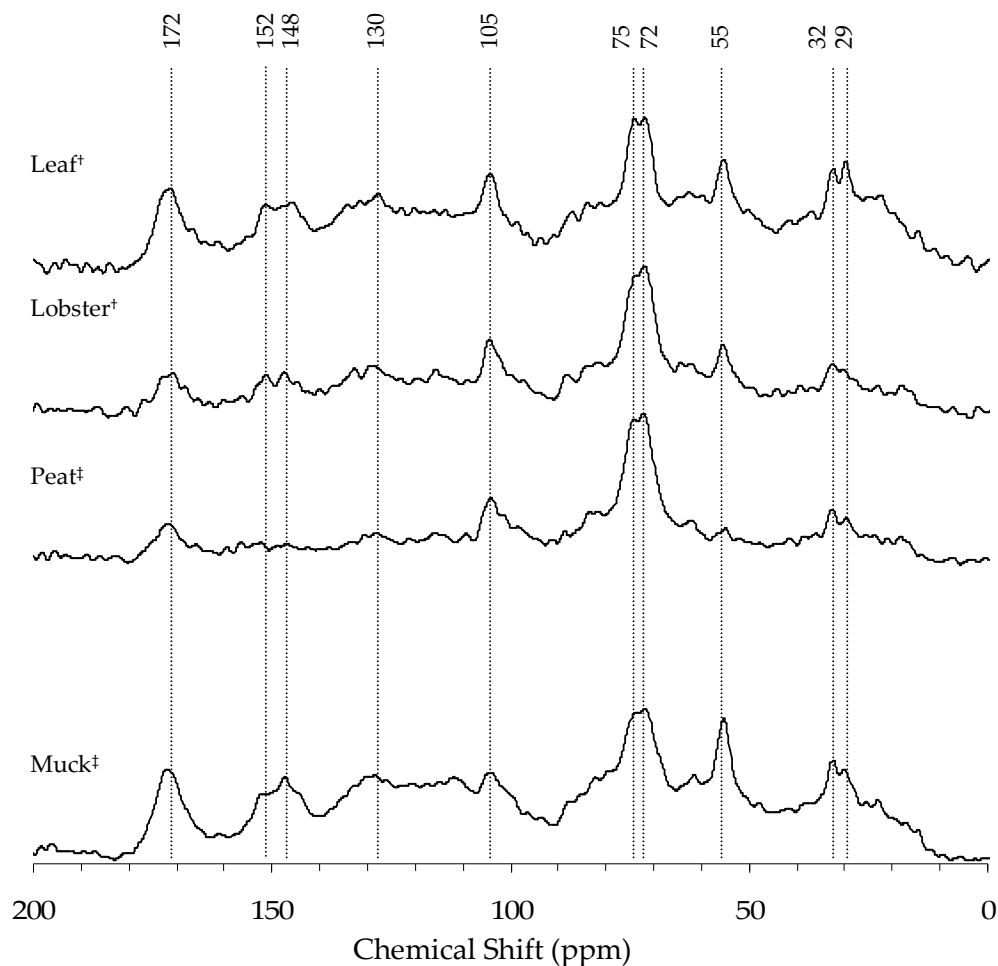


Figure 3.2. The solid-state  $^{13}\text{C}$  NMR spectra of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

Table 3.11. Integration of the CPMAS  $^{13}\text{C}$  NMR spectra<sup>a</sup> for the two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Distribution percent of C chemical shift (ppm) |       |       |        |         |         |         |         | Aliphatic C % | Aromatic C% | Paraffinic C% |
|----------------------|--|-------|-------|--------|---------|---------|---------|---------|---------------|-------------|---------------|
|                      | 0-50   | 50-61 | 61-96 | 96-109 | 109-145 | 145-163 | 163-190 | 190-220 |               |             |               |
| Lobster <sup>†</sup> | 16.1   | 7.9   | 33.6  | 9.5    | 19.9    | 6.6     | 5.6     | 0.8     | 72            | 28          | 17            |
| Leaf <sup>†</sup>    | 22.8   | 8.9   | 25.7  | 8.0    | 20.7    | 7.5     | 6.4     | 0.0     | 70            | 30          | 24            |
| Muck <sup>‡</sup>    | 18.1   | 9.3   | 26.4  | 8.0    | 22.9    | 7.6     | 7.1     | 0.6     | 67            | 33          | 20            |
| Peat <sup>‡</sup>    | 18.9   | 5.7   | 38.6  | 10.0   | 13.8    | 4.7     | 6.2     | 1.9     | 80            | 20          | 21            |

<sup>a</sup> Aliphatic C: Aliphatic C region (0-109 ppm) divided by aliphatic and aromatic regions (0-163 ppm); Aromatic C: aromatic C region (109-163 ppm) divided by aliphatic and aromatic regions (0-163 ppm); Paraffinic C: paraffinic C region (0-50 ppm) divided by aliphatic and aromatic regions (0-163 ppm).

### Conclusions

The results of the physio-chemical characterization illustrate a variety of marked differences between the four organic materials. The comparatively higher total and extractable nutrient content of the composts could have negative consequences should these materials be subjected to the saturated anaerobic conditions of wetland environments. Specifically, high releases of phosphorus could lead to problems with eutrophication and the possible release of toxic levels of manganese by the lobster compost would be detrimental to wetland plant growth. If the high mineral content of the composts is not accounted for in the construction of the mitigation wetland soil, it may have a negative impact on the creation of mitigation wetlands. Higher mineral content would result in lower water holding capacity, lower carbon content and reduction of organic matter functional groups responsible for the retention of certain environmental pollutants.

Results from the elemental, ATR-FTIR, and CPMAS  $^{13}\text{C}$  NMR analyses indicated significant differences in the chemical and structural composition of the different organic materials. The wetland soils have a higher polarity than the composts. The polarity of the compost materials appears to be attributed to the presence of phenolic groups such as tannins. Whereas the polarity of the wetland soils is accredited to the higher polysaccharide content illustrated by the ATR-FTIR and NMR spectra. All four materials were comprised mainly of aliphatic C with low percentages of aromatic C. The peat soil had the highest percentage (80%) of aliphatic C. The aliphatic C content of the composts and the muck soil were comparable, ranging from 67% to 72%. Overall, the differences among the four organic materials illustrated the effect of source material on the chemical, structural, and molecular qualities of the organic materials. These key differences will affect the behavior of the materials within a wetland environment.

## CHAPTER 4

### NUTRIENT RELEASE STUDIES

#### Introduction

One of the important ecological functions of wetland soils is the supply of plant nutrients. In general, natural wetland systems tend to be nutrient poor compared to their upland counterparts (Mitsch and Gosselink, 2000). Decreased nutrient levels are due in part to the diminished mineralization of organic material and subsequent release of plant nutrients under saturated and anaerobic conditions. In addition, wetlands have been attributed with reducing the nutrient concentrations of incoming waters. Nitrate removal is largely accredited to denitrification, which occurs under anaerobic conditions (Reddy et al., 1980). Phosphorus removal from water has been attributed to sorption by sediments and organic matter (Woltemade, 2000). The nutrient removal capacity of natural wetlands is of particular importance as wetland systems are often adjacent to waterways susceptible to eutrophication. As such, the balance between plant nutrient supply and excess nutrient removal may be a delicate one. Moreover, the nutrient dynamics within natural wetlands may vary with seasonal fluctuations in hydrology.

Studies have shown that phosphorus sorption levels vary under aerobic and anaerobic conditions (Patrick and Khalid, 1974; Khalid et al., 1977; Pant and Reddy, 2001). Contrary to previous conclusions, recent studies have reported that natural wetlands may function as phosphorus sources (Moore et al., 1992; Pant and Reddy, 2001; Novak et al., 2004). The function of freshwater wetlands as phosphorus sources rather than sinks is dependent on factors such as phosphorus concentrations along the

sediment-floodwater interface, phosphorus sorption capacity of the wetland soils, microbial and algal activity, and floodwater pH (Logan, 1982; Froelich, 1988). The ability of freshwater wetlands to function as phosphorus sinks decreases with time as the phosphorus sorption capacity of wetland soils is finite (Bridgham et al., 2001). The conversion of agricultural lands to wetland ecosystems to reduce agricultural nonpoint source pollution has become a common practice in recent years. D'Angelo and Reddy (1994) and Pant et al. (2002) have reported an initial release of phosphorus from flooded agricultural soils.

Both Federal and Massachusetts wetland mitigation guidelines recommend the use of low nutrient content organic amendments, but no actual nutrient maxima have been set. Needless to say, maximum nutrient levels require additional study. This portion of the overall study examines the nutrient release from two composts and two wetland soils and evaluates the materials themselves as possible sources of nitrogen and phosphorus.

### **Materials & Methods**

Four different organic materials were evaluated: a leaf compost, a lobster compost, a native muck soil, and a native peat soil. The organic materials were homogenized, air-dried, passed through a 2-mm sieve, homogenized again and stored in air-tight containers at 4°C. All glassware and plasticware was cleaned with a low phosphorus detergent, acid-washed with a 1:1 HCl:deionized water solution and air-dried prior to utilization.

## **Phosphorus Release**

The release of phosphorus from the four organic materials was determined using a modification of the methodology presented by Pant et al. (2002). Preliminary tests were performed to determine the appropriate solid:water ratio that yielded saturated conditions with sufficient excess solution for filtration and analysis. Two-gram samples were placed into polypropylene centrifuge tubes and 40-mL of a dilute 0.1M  $\text{CaCl}_2$  solution was added to normalize ionic strength. Since natural wetlands may undergo alternating cycles of aerobic and anaerobic conditions, the release of phosphorus under both aerobic and anaerobic conditions was analyzed and compared. Aerobic samples were collected after a 1-hour extraction period on a reciprocal shaker (75 strokes per minute). Suspensions were then centrifuged, the supernatant filtered through a 0.45- $\mu\text{m}$  filter and the filtrates were analyzed for orthophosphate concentrations using the EPA approved Ascorbic Acid Method (HACH method 8048, HACH Company, Loveland, CO).

To determine phosphorus release under anaerobic conditions, organic materials were placed into borosilicate glass vials and saturated with a 0.1M  $\text{CaCl}_2$  solution using the same solid: solution ratio described for the aerobic studies. Vials were then capped with air-tight rubber septa and purged with  $\text{N}_2$  gas. The vials were purged weekly with  $\text{N}_2$  gas for 2-minutes to ensure anaerobic conditions. After a 28-day incubation period, the supernatants were separated by centrifuge. The samples were filtered through a 0.45- $\mu\text{m}$  filter within an anaerobic chamber and acidified with one drop of concentrated  $\text{H}_2\text{SO}_4$ . The aliquots were then analyzed for orthophosphates as previously described.



All experiments were performed in triplicate. Data were subjected to a standard analysis of variance (ANOVA) followed by mean separation if the ANOVA f test indicated significant differences among treatment means (SAS Institute, Inc., 2004).

### **Saturated Nutrient Release**

To study the effect of saturation time on nutrient release from the four organic materials, phosphorus, nitrate, and ammonium levels were measured after 1, 14 and 28 days of saturation. A 1:20 solid:solution ratio was utilized as in the previously described aerobic and anaerobic phosphorus release studies. Samples were weighed and placed into 1-L plastic bottles, the 0.1M CaCl<sub>2</sub> solution was added, the bottles thoroughly mixed by hand in an end-over-end manner and placed in an incubator set at 20°C. 100-mL aliquots were collected by pipette, filtered through a 0.45-μm filter and the filtrates were analyzed for orthophosphate concentrations as previously described; nitrate-N by HACH Method 8192 (cadmium reduction method); and ammonium-N by HACH Method 399 (Nessler's methods). The amount of solution collected after each saturation period was subtracted from the initial volume of solution to adjust final nutrient concentrations for decreasing total volumes.

All experiments were performed in triplicate. Data were subjected to a standard analysis of variance (ANOVA) followed by mean separation if the ANOVA f test indicated significant differences among treatment means (SAS Institute, Inc., 2004).

### **Results & Discussion**

For all nutrient release studies, the compost samples were significantly different from the wetland soil samples. More importantly, the compost samples released higher

concentrations of phosphorus, nitrate, and ammonium as compared to the wetland soil samples.

### **Phosphorus Release**

Orthophosphate release was significantly greater for the compost samples as compared to the soil samples under both aerobic and anaerobic conditions (Figure 4.1 and Figure 4.2). The highest orthophosphate release under both aerobic and anaerobic conditions was by the leaf compost, 29.9 and 708 mg kg<sup>-1</sup>, respectively. By contrast, the lowest orthophosphate release under aerobic conditions was from the wetland soils (0.6 and 0.4 mg kg<sup>-1</sup>, for the peat soil and muck soil, respectively). Under anaerobic conditions, orthophosphate release was again lowest from the wetland soils (2.1 and 1.7 mg kg<sup>-1</sup> for the peat soil and muck soil, respectively). It is important to note that under both aerobic and anaerobic conditions the compost samples were significantly different from each other as well as from the wetland soil samples, which were not significantly different from each other.

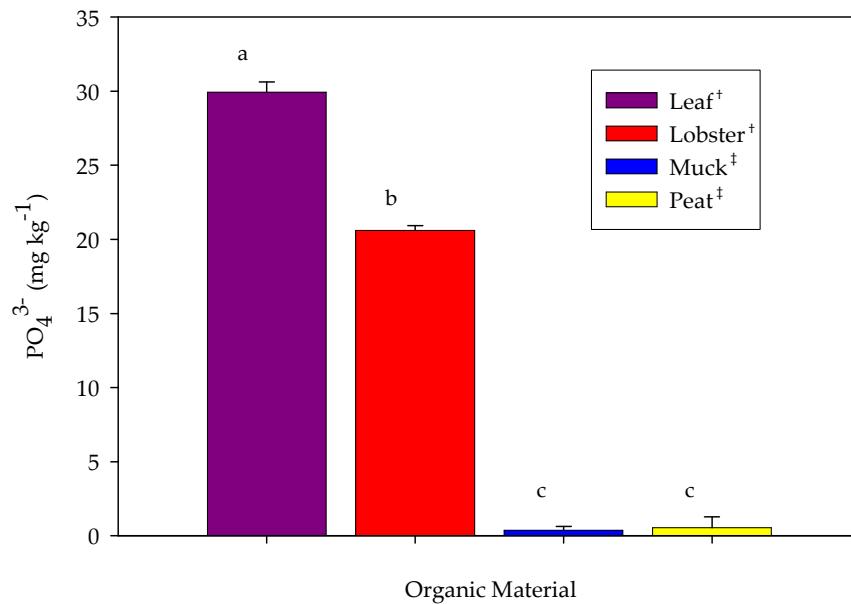


Figure 4.1. Orthophosphate release by two composts<sup>†</sup> and two wetland soils<sup>‡</sup> under aerobic conditions. Columns with the same letter are not significantly different at the  $p=0.01$  probability level according to Duncan's New Multiple Range Test.

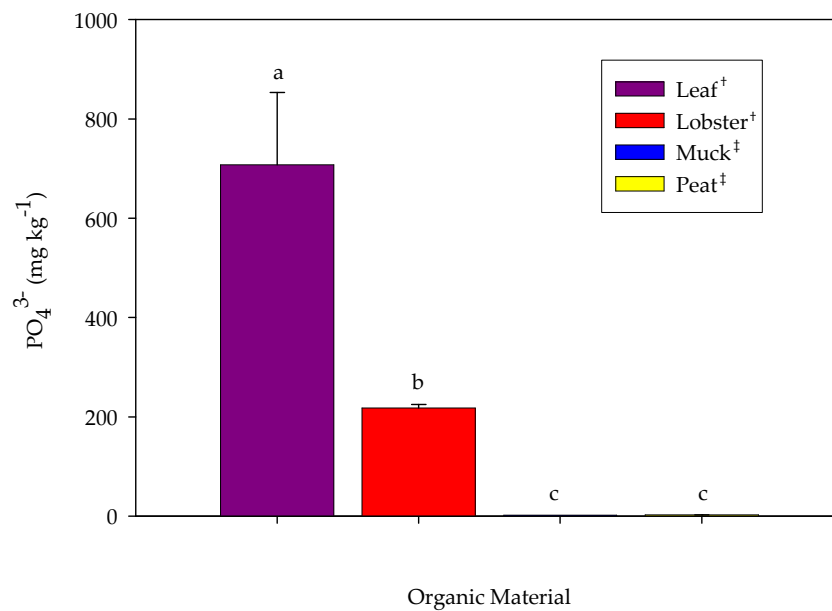


Figure 4.2. Orthophosphate release by two composts<sup>†</sup> and two wetland soils<sup>‡</sup> under anaerobic conditions. Columns with the same letter are not significantly different at the  $p=0.01$  probability level according to Duncan's New Multiple Range Test.

The exceptionally high levels of orthophosphate being released by the composts (particularly under anaerobic conditions) could lead to eutrophic levels within adjacent aquatic systems if these materials were used in mitigation wetlands. Based on the solid:solution ratio utilized in this study, the mean aerobic orthophosphate solution concentrations for the organic materials were 0.04 mg L<sup>-1</sup>, 0.03 mg L<sup>-1</sup>, 1.62 mg L<sup>-1</sup>, and 2.35 mg L<sup>-1</sup> for the peat soil, muck soil, lobster compost, and leaf compost, respectively. The mean anaerobic orthophosphate solution concentrations were 0.31 mg L<sup>-1</sup>, 0.26 mg L<sup>-1</sup>, 32.7 mg L<sup>-1</sup>, 106 mg L<sup>-1</sup> for the peat soil, muck soil, lobster compost, and leaf compost, respectively. Reported levels of orthophosphate released from natural wetlands range from 0.029 to 0.30 mg L<sup>-1</sup> (Sallade and Sims, 1997b; Novak et al., 2004). The concentrations of orthophosphate released by the wetland soils in this study are comparable to levels reported for natural wetland systems. These levels are drastically lower than the levels released from the compost materials in this study. It is important to note that the P concentrations measured in this study are strongly influenced by the solid:solution ratio used for the analysis (i.e. an increase in solution volume would decrease concentration proportionally). Consequently, it is not possible to make a direct comparison with natural systems. However, it is clear that there are significant differences in the P release properties of the organic materials evaluated in this study. These differences suggests that the incorporation of these compost materials into a wetland environment (i.e. mitigation or replication wetland) could lead to excessive levels of phosphorus being released, resulting in negative ecological impacts. It should also be noted that phosphorus release was greater under anaerobic conditions for all

samples which concurs with previous studies (Pant and Reddy, 2001; Moore et al., 1992). Increases in phosphorus release under anaerobic conditions have been attributed to the reduction of ferric ( $\text{Fe}^{3+}$ ) iron to ferrous ( $\text{Fe}^{2+}$ ) iron and the subsequent release of phosphorus from Fe-P complexes.

### **Saturated Nutrient Release**

The release of nutrients with increased saturation time was examined to evaluate a possible “first-flush” phenomenon (1-day samples), as well as the overall effect of saturation time on nutrient release (14 and 28-day samples). The 14-day and 28-day sampling times were selected from a regulatory perspective to represent saturation for “a significant period during the growing season”, which is the regulatory language for meeting the threshold of minimum wetland hydrology.

The release of orthophosphate from all samples increased with increasing saturation time (Figure 4.3). At the 1-day period there was no significant difference between the samples. At both 14-days and 28-days, the composts were significantly different from each other as well as from the soil samples. For all saturation times, the soil samples were not significantly different from each other. These results follow the same trend as the previous aerobic and anaerobic P-release experiments. Similarly, the leaf compost had the highest levels of orthophosphate release at 14-days and 28-days,  $153 \text{ mg kg}^{-1}$  and  $243 \text{ mg kg}^{-1}$ , respectively. Presumably the amount of phosphorus released increased as the organic materials became more saturated and anaerobic. First, aerobic micro-sites were occupied by solution increasing the overall area saturated. Secondly, as the extent and duration of anaerobiosis increased, the use of alternative electron acceptors such as

ferric iron increased. As previously stated, this reduction of iron may lead to the dissolution of Fe-P complexes.

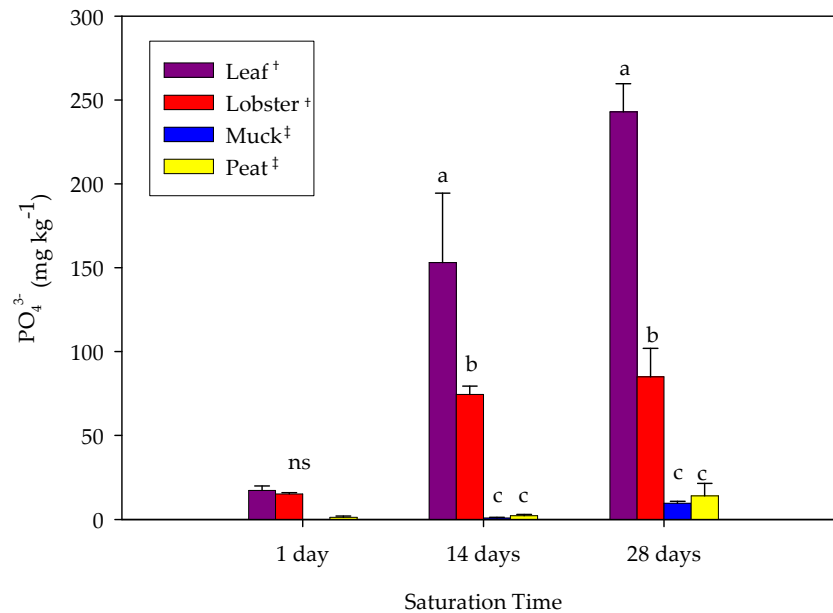


Figure 4.3. Orthophosphate release by two composts<sup>†</sup> and two wetland soils<sup>‡</sup> under varying saturation periods. Columns with the same letter within each time period are not significantly different at the  $p=0.01$  probability level according to Duncan's New Multiple Range Test.

The opposite trend was observed for nitrate release (Figure 4.4). The highest levels of nitrate release occurred at the 1-day sampling period. Nitrate release levels decreased with increasing saturation time. Presumably, nitrate was removed via the microbially mediated conversion of nitrate to  $N_2$  gas. Denitrification occurs at higher rates under saturated and anaerobic conditions (Lowrance et al., 1984; Jordan et al., 1993; Flite et al., 2001). For all saturation times the compost samples had the highest level of nitrate release and were significantly different from the soil samples. The observed "first-flush" phenomenon is of particular concern in a wetland environment as excessively high levels of nitrate may lead to eutrophication. In the case of a newly

established mitigation wetland, this apparent “first-flush” would most likely occur in the absence of a vegetative cover. A single day after creation, any hydrophytes seeded or planted into the mitigation wetland would lack productive root systems. As such, the uptake of nitrate by plants would be drastically limited. While a portion of nitrate may be adsorbed to anion exchange sites or utilized by microbes, it is likely that a large portion would remain in the soil solution and be subject to leaching or lateral movement. Hunter and Faulkner (2001) reported lower denitrification potentials in restored wetlands as compared to natural wetlands. Wang and Bettany (1995) reported nitrate leaching from soils at field capacity.

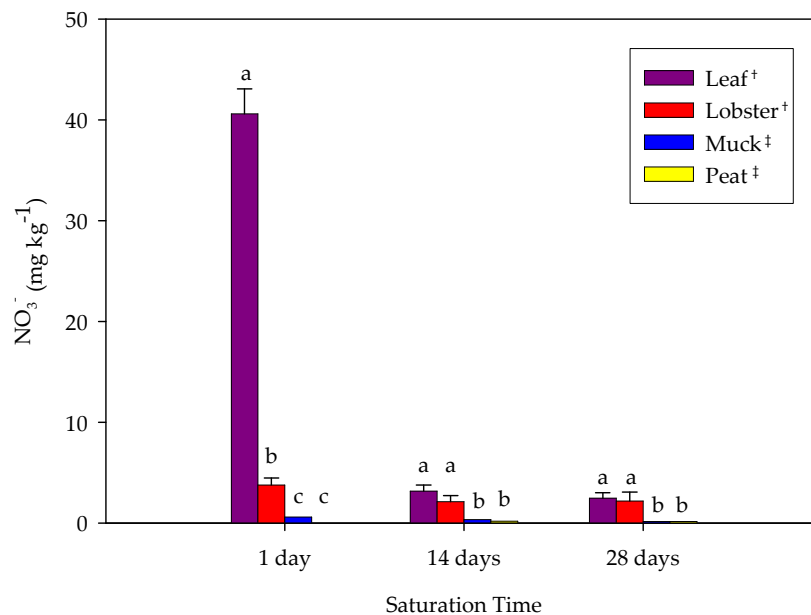


Figure 4.4. Nitrate release by two composts<sup>+</sup> and two wetland soils<sup>+</sup> under varying saturation periods. Columns with the same letter within each time period are not significantly different at the  $p=0.01$  probability level according to Duncan’s New Multiple Range Test.

Ammonium release by the organic materials increased with saturation time (Figure 4.5). Ammonium release was more variable among the samples as compared to orthophosphate and nitrate release. At the 1-day sampling period, the peat soil had the highest ammonium levels. The remaining three samples were not significantly different. The greatest variability was observed at the 14-day sampling period. This is most likely due to the establishment of chemical equilibration of the materials as micro-sites became saturated and anaerobic. At the 28-day period the variability decreases, with the lobster compost releasing the highest amount of ammonium. The remaining three samples were not significantly different. The increase in ammonium levels with time can be attributed to a decrease in nitrification, a continuation of ammonification, or a combination of both processes. As micro-sites became saturated and oxygen was removed, nitrification would decrease dramatically. The creation of ammonium from organic nitrogen (ammonification) is slowed under anaerobic conditions, but not necessarily to the extent of nitrification. The broad group of heterotrophs capable of producing ammonium is not as sensitive to oxygen levels as nitrifying bacteria (Brady and Weil, 1999). As such, the creation of ammonium via ammonification would exceed the loss of ammonium via nitrification or volatilization. Ammonium levels have been shown to increase with increased flooding time and anaerobiosis, and these increases were attributed to a reduction in nitrification (Moore et al., 1992; Wang and Bettany, 1995).



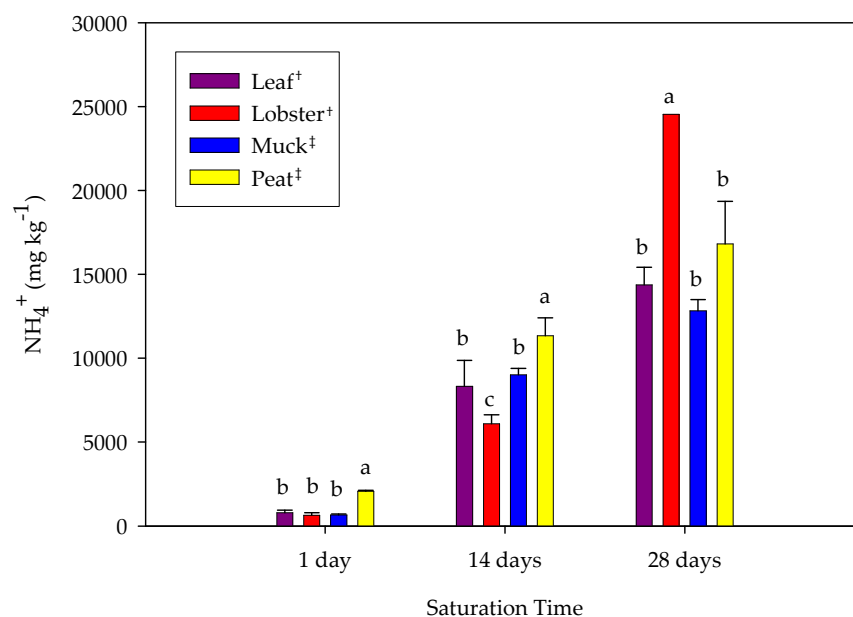


Figure 4.5. Ammonium release by two composts<sup>†</sup> and two wetland soils<sup>‡</sup> under varying saturation periods. Columns with the same letter within each time period are not significantly different at the  $p=0.01$  probability level according to Duncan's New Multiple Range Test.

### Conclusions

For all nutrient release studies, the compost samples were significantly different from the wetland soil samples. More importantly, the compost samples released higher concentrations of phosphorus, nitrate, and ammonium as compared to the wetland soil samples. Previously reported phosphorus release levels from natural wetland systems, constructed wetlands, and flooded agricultural fields range from 0.003 to 7.8 mg  $\text{PO}_4^{3-} \text{L}^{-1}$  (Duxbury and Peverly, 1978; Moore et al., 1992; Corstanje and Reddy, 2004; Novak et al., 2004; Dunne et al., 2005; Aldous et al., 2005). While the majority of phosphorus release observed during this study fell within reported ranges, the release of phosphorus from the compost samples under anaerobic conditions was orders of magnitude higher (32.7 and 106 mg of  $\text{PO}_4^{3-} \text{L}^{-1}$  for the lobster and leaf composts, respectively). Likewise, the

initial release of nitrate by the compost samples was higher than nitrate levels typically observed in natural wetland systems. A “first-flush” of nitrate during the initial construction of mitigation wetlands may result in excessive nitrate levels within adjacent surface waters as it is unlikely that a hydrophilic plant community will be established and able to take up these nutrients. Overall, the results of the study indicate that composts should be carefully examined (i.e. analyzed) prior to their utilization as organic amendments in mitigation wetlands, as certain composts may contribute to excessively high levels of nutrients as compared to native organic wetland soils.

## CHAPTER 5

### NONPOINT SOURCE POLLUTION RETENTION STUDIES

#### Introduction

A primary function of freshwater wetlands is to protect downstream aquatic environments from harmful nonpoint source pollutants. Excessive levels of pollutants within aquatic systems, including nutrients and herbicides, have detrimental effects such as reduced oxygen levels, aquatic life mutations and/or death, and unsafe drinking water. One of the predominant concerns regarding the creation of mitigation wetlands is that these systems may not successfully perform pollutant retention functions as well as natural wetlands. The retention of phosphorus by natural wetlands has been attributed to chemical (precipitation and sorption), biological (plant and microbial uptake), and physical processes (sedimentation) (Gale et. al., 1994; Reddy et al., 1999). In alkaline wetland soils, inorganic phosphorus can complex with calcium and magnesium forming insoluble precipitates (Moore and Reddy, 1994; Reddy et al., 1999; Pant et al., 2002). In acidic wetland soils, inorganic phosphorus can be adsorbed onto non-crystalline iron and aluminum oxides (Patrick and Khalid, 1974; Richardson, 1985; Sanyal and De Datta, 1991; Moore and Reddy, 1994). In organic wetland soils, inorganic phosphorus can react with iron and aluminum associated with organic matter (Guppy et al., 2005). However, the presence of organic matter may reduce inorganic phosphorus retention via competitive sorption to iron and aluminum oxides and the inhibition of iron and aluminum oxide crystallization (Appelt et al., 1975; Bhatti et al., 1998). Studies

have shown that phosphorus sorption levels vary under aerobic and anaerobic conditions (Patrick and Khalid, 1974; Khalid et al., 1977; Pant and Reddy, 2001).

Similarly, natural wetland systems have been attributed with reducing the level of harmful herbicides in surface waters. More specifically, the retention of the commonly used herbicide 2,4-D (2,4-dichlorophenoxy acetic acid) has been ascribed to the process of sorption by organic matter. The sorption of 2,4-D is highly pH dependent. Under acidic conditions, 2,4-D is present in molecular form resulting in increased retention. However, due to its low  $pK_a$  value (2.8), 2,4-D is commonly in anionic form within the pH-ranges typical of freshwater wetlands. As such, the retention of 2,4-D is largely due to ionic sorption by positively charged soil components such as organic matter and hydroxyl-iron and aluminum compounds (Huang et al., 1977; Spadotto and Hornsby, 2003). This portion of the overall study examines the sorption of phosphorus and 2,4-D by different organic materials and evaluates the nonpoint source pollutant retention abilities of the materials.

### **Materials & Methods**

Four different organic materials were evaluated: a leaf compost, a lobster compost, a muck soil, and a peat soil. The organic materials were homogenized, air-dried, passed through a 2-mm sieve, homogenized once more and stored in air-tight containers at 4°C. Prior to the 2,4-D sorption studies, the organic materials were passed through a 500-micron sieve to ensure that sorption was studied for the same fraction as for  $^{13}\text{C}$ -NMR, ATR-FTIR, and elemental analyses (Chapter 3). Prior to the phosphorus sorption experiments, all glassware was cleaned with a low phosphorus detergent, acid-

washed with 1:1 HCl:deionized water solution, triple-rinsed with deionized water and air-dried prior to utilization. Prior to the 2,4-D sorption experiments, all glassware was cleaned with a low phosphorus detergent, rinsed with methanol, triple-rinsed with deionized water, and air-dried prior to utilization.

### **Phosphorus Sorption**

Batch incubation experiments were performed to determine phosphorus sorption under aerobic and anaerobic conditions (Pant and Reddy, 2001). Preliminary studies were performed to determine the appropriate solid:solution ratio for each of the organic materials. The sorbent masses were chosen to achieve 30 to 80% sorption. Sorption experiments were conducted using 40-mL glass centrifuge vials. Thirty milliliters of 0.01M  $\text{CaCl}_2$  background solution containing 0, 0.5, 2, 5, 10, 15, 20, 30, 40, and 50 mg P L<sup>-1</sup> as  $\text{KH}_2\text{PO}_4$  were added to each of the samples. The samples were sealed with teflon screw caps and placed on a reciprocal shaker (75 strokes per minute). A 24-hr equilibrium time as established by previous studies was utilized (Nair et al., 1984; Pant and Reddy, 2001; Pant et al., 2002). A biocide was not applied as the release of phosphorus from microbial populations by the lysing of cell walls has been shown to increase phosphorus levels in solution (Reddy et al., 1998). The supernatants were separated by centrifuge at 3000 g for 15 min, filtered to 0.45 $\mu\text{m}$ , acidified with one drop of concentrated  $\text{H}_2\text{SO}_4$ , and analyzed for orthophosphate concentrations using the EPA approved Ascorbic Acid Method (HACH method 8048, HACH Company, Loveland, CO). Phosphorus not recovered in solutions was considered as the amount adsorbed by the organic materials.

To study phosphorus sorption under anaerobic conditions, samples were placed in 40-mL glass centrifuge vials with 27-mL of 0.01M CaCl<sub>2</sub> background solution. The vials were then capped with air-tight septa and purged with N<sub>2</sub> gas. The vials were purged weekly with N<sub>2</sub> gas for 2-minutes to ensure anaerobic conditions. After a 28-day incubation period, 3mL of 0, 5, 20, 50, 100, 150, 200, 300, 400, and 500 mg P L<sup>-1</sup> prepared in background solution were added to the respective centrifuge tube by syringe (to obtain the final concentrations of 0, 0.5, 2, 5, 10, 15, 20, 30, 40, and 50 mg P L<sup>-1</sup>). The samples were then placed on a reciprocal shaker (75 strokes per minute) for a 24-hr equilibrium, and the supernatants were separated by centrifuge. The samples were filtered through a 0.45-μm filter within a N<sub>2</sub> environment and acidified with one drop of H<sub>2</sub>SO<sub>4</sub>. The aliquots were then analyzed for orthophosphates as previously described.

All experiments were performed in duplicate. Blanks without phosphorus were used for comparison. Centrifuge tubes containing phosphorus without organic matter were used to determine adsorption to the tube surface.

The sorption capacity was calculated using the Langmuir isotherm model:

$$S_T = S_0 + (kS_{\max}C_t)/(1 + kC_t),$$

where  $S_T$  is the total amount of phosphorus adsorbed (mg kg<sup>-1</sup>),  $S_0$  is the initial amount of phosphorus present in the adsorbed phase (mg kg<sup>-1</sup>),  $k$  is the sorption constant related to the binding energy (L mg<sup>-1</sup>),  $C_t$  is the equilibrium concentration of phosphorus in solution after 24 hours (mg L<sup>-1</sup>), and  $S_{\max}$  is the maximum amount of phosphorus adsorbed (mg kg<sup>-1</sup>).  $S_0$ ,  $S_{\max}$ , and  $k$  were estimated using the SigmaPlot curve-fitting routine (Litaor et al., 2005).

The equilibrium phosphorus concentration,  $EPC_0$ , was calculated using the Temkin isotherm model as follows (Vandenhove et al., 1998; Barrow, 1999):

$$S = a \times \ln (C_t/b),$$

where  $a$  is a coefficient related to buffering capacity and  $b$  is a constant for a soil in its actual state. The constant  $b$  represents the  $EPC_0$  when  $S = 0$ . As such the previous equation can be written as:

$$S = a \ln(C_t/EPC_0)$$

The parameters  $a$  and  $EPC_0$  were estimated using the SigmaPlot curve-fitting routine (Litaor et al., 2005).

Given the previously described pH dependent nature of phosphorus sorption, solution subsamples were taken after the equilibrium period to monitor pH using a glass electrode-calomel electrode pH meter (Fisher Accumet model #805).

### **2,4-D Sorption**

The organic materials were treated with  $^{14}\text{C}$ -labeled (radioactive purity >99%) and unlabeled 2,4-D purchased from Sigma Aldrich Chemical Co (St Louis, MO). 2,4-D is an acidic phenoxy herbicide commonly used to control broadleaf weeds in agricultural, residential, and aquatic environments (Boivin et al., 2005). Selected properties of 2,4-D include: molecular formula,  $\text{C}_{14}\text{H}_{20}\text{ClNO}_2$ ; molecular weight, 221.04 g  $\text{mole}^{-1}$ ; pKa, 2.8; octanol-water partitioning coefficient ( $K_{ow}$ ), 2.58-2.83; aqueous solubility, 311 mg  $\text{L}^{-1}$ ; aerobic half-life, <7 days; and U.S. EPA MCL, 0.07 mg  $\text{L}^{-1}$ .

2,4-D sorption studies were performed using a batch equilibrium technique at room temperature (Xing and Pignatello 1997; Xing, 2001). Sorption experiments were

conducted using 15-mL glass centrifuge vials with aluminum liners. A 0.01M  $\text{CaCl}_2$  solution was used to normalize ionic strength (Xing, 2001). Sodium azide, ( $\text{NaN}_3$ ), was added to the background solution to prohibit microbial growth (Xing, 2001) and the background solution was adjusted to pH 7. Given the previously described pH dependent nature of 2,4-D sorption, solution subsamples were taken after the equilibrium period to monitor pH using a glass electrode-calomel electrode pH meter (Fisher Accumet model #805).

Preliminary ratio experiments were performed and the sorbent masses were chosen to achieve 30 to 80% sorption. Isotherms were comprised of 10 concentration points. All points, including the blank, were run in duplicate. Initial concentrations ranged from 0.1 to 100 ppm. Preliminary kinetics tests were performed to determine the time of apparent equilibrium between each sorbate-sorbent combination. Results concurred with previous studies which indicated a 24-hr equilibrium time (Farenhorst et al., 2001; Spadotto and Hornsby, 2003). The vials were sealed with aluminum foil-lined Teflon screw caps, placed in a cardboard box to inhibit photodegradation, and placed on a reciprocal shaker (75 strokes per minute) for 24 hours. The vials were centrifuged at 3000  $g$  for 20 minutes. A 1.2-mL aliquot of supernatant was added to 6 mL of Scintiverse cocktail (Fisher Scientific, Pittsburg, PA). Concentrations of  $^{14}\text{C}$ -labeled 2,4-D in solution were measured using a scintillation counter (Beckman LS6500, Fullerton, CA). Blanks without 2,4-D were used for comparison. Centrifuge tubes containing 2,4-D without organic matter were used to determine adsorption to the tube surface. Due to negligible



sorption of 2,4-D by the vials and no biodegradation, the concentrations of 2,4-D sorbed were calculated by mass difference.

Sorption data were fitted to the Freundlich isotherm:

$$S = K_F C^N,$$

where  $S$  is the total sorbed 2,4-D ( $\mu\text{g g}^{-1}$ ), and  $C$  is the equilibrium concentration ( $\mu\text{g mL}^{-1}$ ). The sorption parameters  $K_F$ , the Freundlich sorption capacity coefficient [ $(\mu\text{g g}^{-1})/(\mu\text{g mL}^{-1})^N$ ], and  $N$ , indicating isotherm non-linearity (dimensionless), were determined by linear regression of log-transformed data.

In addition, the  $K_{OM}$  was calculated using the following equation to determine the distribution sorption coefficient per unit of organic matter:

$$K_{OM} = \frac{K_F}{\% \text{ OM}} \times 100$$

## **Results & Discussion**

### **Phosphorus Sorption**

#### **Aerobic Phosphorus Sorption Maxima**

Under aerobic conditions the wetland soils sorbed greater amounts of phosphorus than the compost samples (Table 5.1). Increased levels of P sorption have been positively correlated with the presents of  $\text{Fe}^{3+}$  oxides and hydroxides under aerobic conditions (Richardson, 1985; D'Angelo and Reddy, 1994; Hogan et al., 2004). Under acidic conditions, variable charged minerals such as iron and aluminum oxides and the surface edges of layered silicates may provide positively charged sites for the adsorption

of inorganic phosphorus. In contrast to reported studies (that evaluated soil/sediments with comparable pH values, 3.5 to 7.6) on constructed wetlands (Dunne et al., 2005; Yoo et al., 2006), altered wetlands (Litaor et al., 2005), and natural wetlands (Reddy et al., 1998), oxalate-extractable aluminum and iron levels were not strongly related to the aerobic sorption maximum of the four organic materials (Table 5.2). This relationship suggests that the percent organic matter had a greater influence on aerobic phosphorus than the presence of iron and aluminum oxides. This suggestion is also supported by the high percentage of organic matter and high aerobic sorption max of the wetland soils as compared to the composts. Different sorption mechanisms may govern under anaerobic conditions.

Table 5.1. Selected aerobic phosphorus sorption parameters of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material     | Selected Aerobic Phosphorus Sorption Parameters |  |                                 |                 |                |
|----------------------|---|--|---------------------------------|-----------------|----------------|
|                      | $S_{\max}^a$<br>mg kg <sup>-1</sup>             | P Binding Energy ( $k$ )<br>L mg <sup>-1</sup> | $EPC_0^b$<br>mg L <sup>-1</sup> | pH <sup>c</sup> | R <sup>2</sup> |
| Lobster <sup>†</sup> | 659 ± 38  | 0.33 ± 0.12                                    | 0.75 ± 0.05                     | 6.56            | 0.9823         |
| Leaf <sup>†</sup>    | 628 ± 18  | 0.20 ± 0.03                                    | 1.08 ± 0.06                     | 6.49            | 0.9976         |
| Muck <sup>‡</sup>    | 1811 ± 163                                      | 0.16 ± 0.04                                    | 0.08 ± 0.02                     | 5.60            | 0.9833         |
| Peat <sup>‡</sup>    | 2976 ± 362                                      | 0.12 ± 0.04                                    | 0.03 ± 0.01                     | 3.31            | 0.9758         |

<sup>a</sup>  $S_{\max}$  is the maximum amount of phosphorus sorbed

<sup>b</sup>  $EPC_0$  is the equilibrium phosphorus concentration, the concentration of phosphorus at which the isotherm crosses the x-axis and sorption equal desorption

<sup>c</sup> pH of the solution after the 24-hr equilibrium period.

Table 5.2. Pearson's correlation values of P sorption attributes with selected soil parameters.

| Selected<br>Parameter | S <sub>max</sub> <sup>a</sup> | EPC <sub>0</sub> <sup>b</sup> |           |
|-----------------------|-------------------------------|-------------------------------|-----------|
|                       | Aerobic                       | Aerobic                       | Anaerobic |
| pH                    | -0.9748*                      | 0.7795                        | 0.7847    |
| %OM                   | 0.9702*                       | -0.9450*                      | -0.9497*  |
| Fe <sub>Ox</sub>      | -0.4822                       | 0.0665                        | 0.0282    |
| Al <sub>Ox</sub>      | -0.6908                       | 0.3377                        | 0.2974    |
| Mn <sub>Ox</sub>      | 0.2499                        | -0.6274                       | -0.6124   |
| P <sub>Ox</sub>       | -0.9626*                      | 0.9613*                       | 0.9655*   |
| P <sub>Morgan</sub>   | -0.8486                       | 0.9957*                       | 0.9954*   |
| P <sub>Total</sub>    | -0.8882                       | 0.9557*                       | 0.9716*   |
| C <sub>Total</sub>    | 0.9551*                       | -0.9487*                      | -0.9567   |
| Polarity              | 0.8789                        | -0.9599*                      | -0.9377   |

\* Significant at the 0.05 probability level

<sup>a</sup> S<sub>max</sub>, phosphorus sorption maximum

<sup>b</sup> EPC<sub>0</sub> net equilibrium phosphorus concentration

### Anaerobic Phosphorus Sorption Maxima

Under anaerobic conditions the lobster compost had a higher sorption max than the wetland soil samples (Table 5.3). The high sorption max value is likely due to the high pH (6.74) value reported for the lobster compost under anaerobic conditions. Moore and Reddy (1994) concluded that Ca rather than Fe was the dominant factor governing P behavior under anaerobic conditions. The fixation of phosphorus by calcium (also magnesium and aluminum) is highly influenced by pH dependent solubility and not reduction-oxidation reactions. Under high pH conditions the sorption of phosphorus can be attributed to the formation of calcium phosphate precipitates such as apatite, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH (Moore and Reddy, 1994; Litaor et al., 2005). The anaerobic leaf sample had the highest pH value (6.91). However, an anaerobic sorption max could not be calculated, as the sorption was only best fit by the Langmuir isotherm at lower

concentrations of added phosphorus (0 to 15 mg L<sup>-1</sup>) (Figure 5.1). The appearance of the overall isotherm suggests a second Langmuir isotherm for the higher concentrations of added phosphorus (20 to 50 mg L<sup>-1</sup>) with a  $S_{\max}$  value near 700 mg kg<sup>-1</sup> (Figure 5.2). However, attempts to fit the higher concentrations to the Langmuir isotherm using SigmaPlot were unsuccessful, resulting in sorption parameters with unrealistic values and high standards errors. It is postulated that were additional concentrations of added phosphorus studied the anaerobic sorption by the leaf compost would have fit the Langmuir isotherm, as the sorption of phosphorus by soils and organic matter is finite (Bridgham et al., 2001). The maximum level of added phosphorus chosen for the sorption experiments represents an environmentally unsound level of phosphorus, magnitudes higher than permissible concentrations under the federal Clean Water Act. Therefore, from the perspective of nonpoint source phosphorus attenuation by mitigation wetlands, the anaerobic sorption by the leaf compost is best fit to the Langmuir isotherm for the concentrations of added phosphorus from 0 to 15 mg L<sup>-1</sup>.

Furthermore, high levels of phosphorus sorption under anaerobic conditions by the lobster compost may be attributed to additional concentrations of amorphous ferrous hydroxides from secondary precipitation. Under high pH conditions hydroxide is abundant in the soil solution and readily available for complexation with ferrous iron. Additionally, lower levels of phosphorus sorption by the wetland soils may be attributed to a lower amount of reactive iron adsorbing surfaces due to the dissolution of ferric phosphates (Moore and Reddy, 1994) as well as the diminished secondary precipitation of ferrous hydroxides under comparatively more acidic conditions.

Table 5.3. Selected anaerobic phosphorus sorption parameters of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material      | Selected Anaerobic Phosphorus Sorption Parameters |   |   |                 |                |
|-----------------------|---|---|---|-----------------|----------------|
|                       | $S_{\max}^a$<br>mg kg <sup>-1</sup>               | P Binding Energy ( <i>k</i> )<br>L mg <sup>-1</sup> | EPC <sub>0</sub> <sup>b</sup><br>mg L <sup>-1</sup> | pH <sup>c</sup> | R <sup>2</sup> |
| Lobster               | 1922 ± 179  | 0.15 ± 0.04   | 0.72 ± 0.06   | 6.74            | 0.9863         |
| Leaf (L) <sup>d</sup> | 416 ± 69  | 0.37 ± 0.47   | 0.97 ± 0.00   | 6.91            | 0.8878         |
| Leaf (H) <sup>d</sup> | ND*   | ND*   | ND*   | 6.91            | ND*            |
| Muck                  | 1547 ± 107  | 0.45 ± 0.12   | 0.01 ± 0.00   | 5.83            | 0.9770         |
| Peat                  | 1539 ± 150  | 0.59 ± 0.23   | 0.02 ± 0.01   | 3.56            | 0.9533         |

<sup>a</sup>  $S_{\max}$  is the maximum amount of phosphorus sorbed.

<sup>b</sup> EPC<sub>0</sub> is the equilibrium phosphorus concentration, the concentration of phosphorus at which the isotherm crosses the x-axis and net sorption equals net desorption.

<sup>c</sup> pH of the solution after the 24-hr equilibrium period.

<sup>d</sup> (L) indicates the anaerobic sorption by the leaf compost at low concentrations of added phosphorus (0 to 15 mg L<sup>-1</sup>). (H) indicates the anaerobic sorption by the leaf compost at low concentrations of added phosphorus (20 to 50 mg L<sup>-1</sup>).

\* ND means not determined.

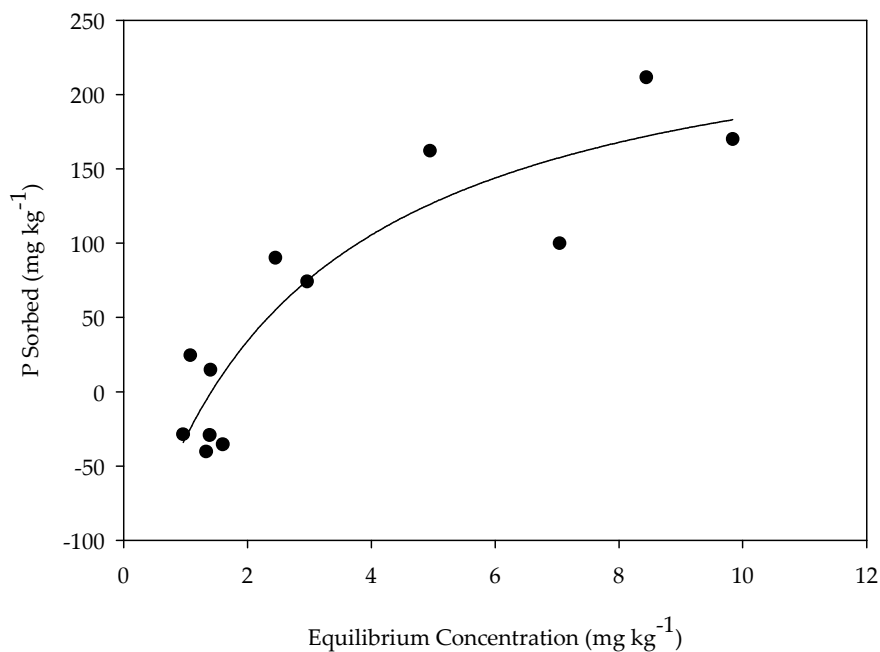


Figure 5.1. Sorption of phosphorus by a leaf compost under anaerobic conditions for low concentrations of added P (0 to 15 mg L<sup>-1</sup>).

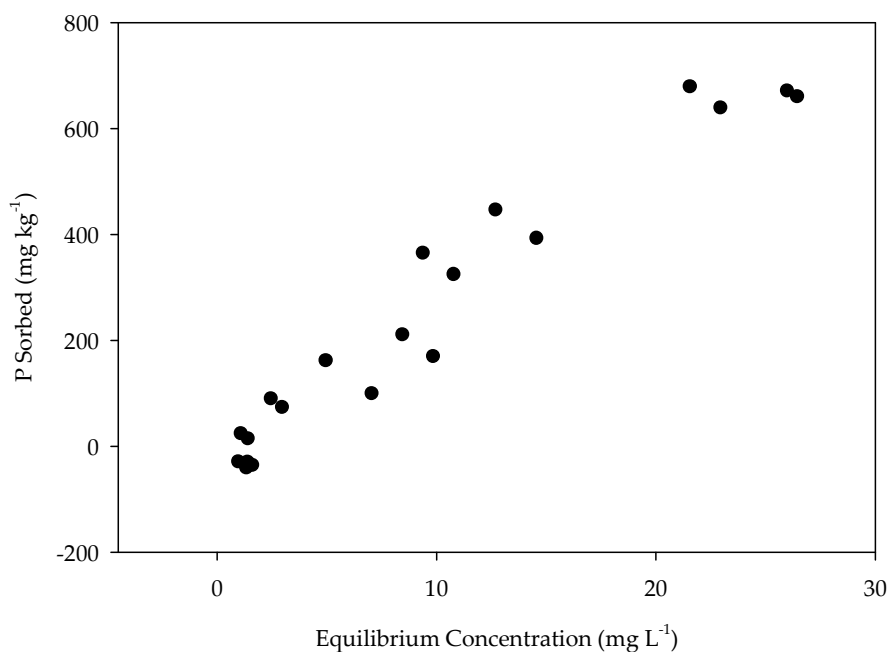


Figure 5.2. Sorption of phosphorus by a leaf compost under anaerobic conditions.

### Organic Matter

Given the high percentage of organic matter within the wetland soil samples, it is likely that phosphorus sorption was enhanced by processes such as metal bridging between organic acids (Guppy et al., 2005). The complexation between aluminum and iron associated with organic matter has been reported for several freshwater wetland ecosystems (Kadlec, 1989; Craft and Richardson, 1993; Pant and Reddy, 2001). Given the high mineral content of the compost samples, the lower aerobic sorption max by the compost samples (in comparison to the wetland soils) indicates that phosphorus sorption by mineral components was lower than the degree of sorption via organic complexation. The effect of organic matter on phosphorus sorption is somewhat contentious. Some studies indicate a reduction of phosphorus sorption with increasing

organic matter content due to competitive sorption and the coating of Fe and Al (Stevenson, 1994). Conversely, other studies have reported an increase in phosphorus sorption with increasing organic matter content due to organo-metal associations (Traina et al., 1986; Kadlec, 1989; Craft and Richardson, 1993; Pant and Reddy, 2001; Guppy et al., 2005). The indirect influence of organic matter via a possible alteration of the crystalline structure and surface areas was suggested by McDowell and Condon (2001). The positive correlation between organic matter content and aerobic  $S_{\max}$  observed during this study indicates that organic matter provided a sorption mechanism rather than hindering sorption (Table 5.2).

## **pH**

The pH values were measured under both aerobic and anaerobic conditions after equilibrium. The data concur with the literature, which states that as reducing conditions continue wetland soil chemistry approaches neutral (Mitsch and Gosselink, 2000). All four organic samples depicted an increase in pH from aerobic conditions to anaerobic. Under aerobic conditions, an inverse relationship between pH and sorption maximum was observed, with the greatest amount of sorption occurring under highly acidic conditions (Table 5.2). This suggests the sorption of inorganic phosphorus by variable charge surfaces (increased anion exchange with decreasing pH), and via metal bridge (Fe and Al) with organic matter. Under highly acid conditions (pH <4), iron and aluminum solution concentrations increase (Richardson and Vepraskas, 2001), allowing a subsequent complexation with organic matter and phosphorus. Under anaerobic conditions the lobster compost demonstrated the greatest  $S_{\max}$ . This suggests the

sorption of phosphorus by Ca compounds. Unlike Fe and Mn, Ca solubility is not affected by redox. Calcium solubility however, is affected by pH. Given the reported pH (6.74) and high total and extractable Ca contents (Chapter 3) it is likely that complexation between Ca and P was a predominant mechanism under alkaline conditions.

### **Net Equilibrium Phosphorus Concentration**

The net equilibrium phosphorus concentration ( $EPC_0$ ) is defined as the concentration of phosphorus in the soil solution at which point no net phosphorus sorption or desorption from the soil phase occurs. From an ecological standpoint, the  $EPC_0$  value for a given substrate has an important implication as to whether the substrate will successfully reduce excessive levels of phosphorus from freshwater systems. The  $EPC_0$  of given substrates may be utilized to determine the direction and size of phosphorus flux from the substrate to the overlaying and adjacent waterbody and vice versa (House and Denison, 2002; Zhou et al., 2005). If the  $EPC_0$  value is lower than the phosphorus concentration in the water the substrate will sorb phosphorus. Conversely, if the  $EPC_0$  value is higher than the phosphorus concentration in the water, the substrate will act as a phosphorus source. Both wetland soil samples had lower mean  $EPC_0$  values as compared to the compost samples under both aerobic and anaerobic conditions (Table 5.1 and Table 5.3). The  $EPC_0$  values for the anaerobic and aerobic lobster compost and the aerobic leaf compost samples were 7 to 10 times higher than the  $0.1 \text{ mg L}^{-1}$  EPA recommended level for phosphorus entering waterbodies, 0.72, 0.75, 0.97 and  $1.08 \text{ mg of P L}^{-1}$ , respectively. This indicates that the selected compost samples will act as phosphorus sources until the phosphorus concentrations in the water



exceed levels that are magnitudes higher than the EPA recommended threshold.

### **Phosphorus Sorption Binding Energy**

The binding energy ( $k$ ) typically indicates the relative diffusion rate of phosphorus from the soil or organic material. As  $k$  values increase, the rate of soluble phosphorus diffusion decreases (Reddy and Rao, 1983; Dunne et al., 2005) as an increase in  $k$  values indicated a stronger sorption of phosphorus by the sorbent. Under aerobic conditions the compost samples had higher  $k$  values as compared to the wetland soil samples (Table 5.1). The low  $k$  values of the aerobic wetland soil samples and the decrease in  $S_{\max}$  under anaerobic conditions indicate a weakly sorbed component of P which is susceptible to redox changes (i.e the reduction of iron and subsequent decrease in ferric oxides and anion exchange). The overall highest  $k$  values were present under anaerobic conditions and were associated with the muck and peat soil samples, 0.45 and 0.59 L mg<sup>-1</sup>, respectively (Table 5.3). This indicates that although the muck and peat soil samples have a lower anaerobic  $S_{\max}$  as compared with the composts, the sorbed phosphorus is retained more tenaciously.

### **2,4-D Sorption**

The sorption of 2,4-D by soil/sediment has been strongly related to pH and organic matter content (Spadotto and Hornsby, 2003; Farenhorst, 2006). Sorption data of 2,4-D to commercially available composts and natural wetland soils fit well to the Freundlich equations (Figure 5.3).  $K_f$  values ranged from 0.95 (leaf compost) to 20.95 (peat soil). The  $K_f$  value of the peat sample is comparable to  $K_f$  values of humic acid and composted straw previously reported by Benoit et al. (1996), 101 and 61, respectively.

Due to their different units, as a result of isotherm nonlinearity ( $N \neq 1$ ), the  $K_f$  values cannot be compared between all organic materials. Nonlinearity has been attributed to organic matter as a dual-mode sorbent (Xing and Pignatello, 1997). As such, to allow comparison, concentration-dependent organic matter normalized sorption coefficients ( $K_{om}$ ) values at two equilibrium concentrations ( $0.2 \mu\text{m mL}^{-1}$  and  $2.0 \mu\text{m mL}^{-1}$ ) were calculated. Normalization using organic matter content as opposed to organic carbon content was chosen based on analytical cost and availability. One of the overall goals of this research is to improve the evaluation of composts as mitigation wetland amendments. Percent organic matter via loss on ignition is a commonly measured compost characteristic, whereas the determination of organic carbon via elemental analysis may be limited by both availability and cost.

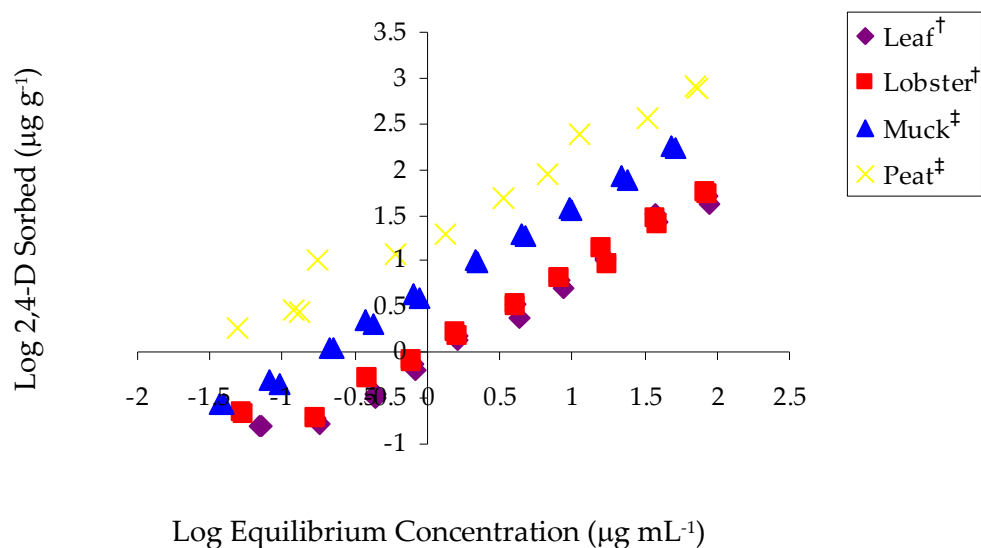


Figure 5.3. Logarithmic trends of 2,4-D sorption to two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

$K_{om}$  values of the four organic materials varied between equilibrium concentrations (Table 5.4), which indicates a high heterogeneity within the samples and concurs with the  $N$  values (all less than 1). Natural soils are widely known as decidedly heterogeneous materials. Similarly, the heterogeneity of the compost samples may be attributed to the variable components (manure, bark, lobster waste etc.) of the lobster composts and the variation in collection sites (vegetation type, location and management practices) in regards to the leaf compost. Therefore, despite the applied homogenizing practice, inherent heterogeneity persisted.

$K_{om}$  values were higher for the natural wetland soils as compared to the compost samples, with the peat soil ( $K_{om} = 29.1$  and  $20.2$ , for  $C_e = 0.2$  and  $2.0$ , respectively) more than 4 times greater than both the leaf and lobster compost. The high  $K_{om}$  value of the peat soil corresponds with the peat soil as the most acidic sample as well as the sample with the greatest percent organic matter. This concurs with studies that have demonstrated greater 2,4-D sorption under acidic conditions where the herbicide is present in molecular form (Weber, 1972; Spadotto and Hornsby, 2003) as well as greater 2,4-D sorption with increased organic matter/organic carbon content (Mcgrath, 1996; Wu et al., 2000; Prado et al., 2001; Dorado et al., 2003; Spadotto and Hornsby, 2003; Picton and Farenhorst, 2004). The effect of pH on the sorption of 2,4-D by the remaining three organic materials may have been minimal as previous studies report no significant correlation between pH and sorption when the difference between the  $pK_a$  (2.73) and the soil pH is greater than two units (Ahrens, 1994; Farenhorst et al., 2001; Gaultier et al., 2006).

Table 5.4. Selected 2,4-D sorption parameters of two composts<sup>†</sup> and two wetland soils<sup>‡</sup>.

| Organic Material | Selected 2,4-D Sorption Parameters |                             |                                    |                                    |                 |                |
|------------------|------------------------------------|-----------------------------|------------------------------------|------------------------------------|-----------------|----------------|
|                  | N <sup>a</sup>                     | K <sub>f</sub> <sup>b</sup> | K <sub>om</sub> <sup>c</sup>       | K <sub>om</sub> <sup>c</sup>       | pH <sup>d</sup> | R <sup>2</sup> |
|                  |                                    |                             | Ce = 0.2<br>(µg mL <sup>-1</sup> ) | Ce = 2.0<br>(µg mL <sup>-1</sup> ) |                 |                |
| Lobster Compost  | 0.8073                             | 1.22 ± 0.30                 | 6.37                               | 4.11                               | 7.19            | 0.9754         |
| Leaf Compost     | 0.8641                             | 0.95 ± 0.03                 | 4.10                               | 2.97                               | 7.12            | 0.9839         |
| Muck             | 0.9068                             | 4.80 ± 0.01                 | 7.30                               | 5.93                               | 5.56            | 0.9980         |
| Peat             | 0.8419                             | 20.95 ± 0.04                | 29.10                              | 20.16                              | 3.78            | 0.9806         |

<sup>a</sup> N is a measurement of isotherm nonlinearity.

<sup>b</sup> K<sub>f</sub> is the sorption capacity coefficient [(µg g<sup>-1</sup>)/(µg mL<sup>-1</sup>)<sup>N</sup>].

<sup>c</sup> K<sub>om</sub> = (S/Ce)/F<sub>om</sub>, where S is the solid phase concentration, C<sub>e</sub> is the liquid phase equilibrium concentration and F<sub>om</sub> is the fraction of organic matter, and is calculated at C<sub>e</sub> = 0.2 and 2.0 µg mL<sup>-1</sup>

<sup>d</sup> pH of the solution after the 24-hr equilibrium period.

Normalization using organic carbon content as K<sub>oc</sub> was performed for literature comparison ( $K_{oc} = (S/C_e)/F_{oc}$ ). K<sub>oc</sub> values were 7.96, 5.96, 12.87, and 49.02 for the lobster compost, leaf compost, muck soil, and peat soil, respectively. Benoit et al., (1996) and Halabicki-Picton (2003) reported that K<sub>oc</sub> values increase with increasing humification. The K<sub>oc</sub> values of compost samples and muck soil fall within the range of K<sub>oc</sub> values reported for lignin, canola straw, pine shaving, and wheat straw (K<sub>oc</sub> values from ~4 to 16). The K<sub>oc</sub> value of the peat soil exceeds this range but is substantially less than K<sub>oc</sub> values reported for more humified substances such as composted straw and humic acid (K<sub>oc</sub> values from 133 to ~250). The pH value reported for the composted straw (6.5) was greater than the peat soil (3.56), whereas the pH value reported for the humic acid (3.3) was comparable. The higher K<sub>oc</sub> value of the humic acid may be attributed to a greater concentration of molecular 2,4-D at a lower pH. However, the concentration of molecular 2,4-D would have been lower for the composted straw given the higher pH, therefore indicating sorption of 2,4-D in the anionic form. This suggests that the

sorption by the composted straw via such phenomenon as positively charged surface areas and cation bridging was greater than the combined sorption of molecular and anionic 2,4-D by the peat sample.

A comparison between the compositions of the four organic materials in relation to 2,4-D sorption is presented in Chapter 6.

### **Conclusion**

Under aerobic conditions the natural organic wetland soils had higher phosphorus  $S_{\max}$  as compared to the commercially available compost samples. Conversely, the  $S_{\max}$  of the lobster compost was higher than the wetland soil under anaerobic conditions. The variation of the natural wetland soils as phosphorus sources and sinks concurs with recent studies, which have documented decreased P sorption under anaerobic conditions (Moore and Reddy, 1994). In contrast, to several published studies (Reddy et al., 1998; Litaor et al., 2005; Dunne et al., 2005; Yoo et al., 2006) oxalate extractable iron, aluminum, and manganese were not strong indicators of P sorption under aerobic conditions. The absence of a strong trend was attributed to the degree of mineral content variation between the compost samples and the wetland soil samples (Chapter 3). An evaluation of trends under anaerobic conditions was prohibited as the sorption of phosphorus by the leaf compost under anaerobic conditions only fit the Langmuir isotherm at low concentrations of added P.

$EPC_0$  values are an important indication of a substrate's ability to reduce excessive amounts of phosphorus from solution. The wetland soil samples had lower  $EPC_0$  values under both aerobic and anaerobic conditions as compared to the compost

samples. In addition, the wetland soil  $EPC_0$  values were lower than the USEPA recommended threshold for phosphorus, indicating that these soils would act as a sink for phosphorus. Conversely, the  $EPC_0$  values for the compost samples ranged from 0.72 to 1.08 mg L<sup>-1</sup>. The compost samples will serve as a phosphorus source until the concentration of solution phosphorus exceeds their  $EPC_0$  values, which are substantially higher than the U.S. EPA recommended threshold for phosphorus.

The sorption of the commonly-used and controversial herbicide, 2,4-D, was greater by the wetland soils as compared to the composts. 2,4-D sorption appeared to be predominantly influenced by pH and organic matter content, with greater sorption occurring at lower pH and higher percent organic matter. An evaluation of 2,4-D sorption in relation to organic matter composition is presented in Chapter 6.

The results of this portion of the overall research demonstrate that the selected commercially available composts behave differently than the wetland soils as sinks for nonpoint source pollutants. Moreover, the selected composts exhibit a lower ability to reduce ecologically adverse concentrations of both phosphorus and 2,4-D. As such, the application of these specific composts in the creation of mitigation wetlands would result in a lack of in-kind replication from the standpoint of the wetland function of reducing nonpoint source pollution.

## CHAPTER 6

### CONCLUSIONS

#### Organic Material Characterization

As hypothesized in Chapter 1, the commercially available composts examined in this study are significantly different in both physical and chemical composition as compared to two natural organic wetland soils and as compared to each other. The composts had significantly higher total nutrients (P, K, B, Zn, Fe, Al, Cd, Ni, Cr) and extractable nutrients (P, K, Ca, B, Mn) as compared to the wetland soils. In addition, the composts were significantly different from each other in regards to the majority of both total and extractable nutrients (Tables 3.2 to 3.7). Nutrient content within natural wetland systems varies greatly depending on factors such as: organic matter content, pH, soil parent material, landscape position and hydrology. As such, nutrient analysis is necessary to determine whether an organic amendment (commercial compost) will mimic the nutrient supplying function of the natural wetland soil being replicated. Based on available literature, the composts examined in this study contain nutrient levels outside the reported ranges for natural wetlands; thus indicating that these composts would not successfully mimic natural wetland soils from a nutrient standpoint, and may provide excessive amounts of nutrients with potentially adverse ecological impacts (Johnston, 1991; Ahn and Mitsch, 2001; Young and Ross, 2001; Corstanje et al., 2006). Potential adverse impacts include: excessive levels of P and a “first flush” of excessive levels of nitrate leading to the eutrophication of adjacent

waterbodies for both composts analyzed and potentially toxic levels of manganese supplied by the lobster compost.

In addition to differences in nutrient content, the selected composts had significantly higher pH values than the wetland soil samples. pH values of the composts (7.70 and 7.56) were comparable to those of alkaline wetland systems (pH values > 7.4), but higher than the more predominant circumneutral freshwater wetlands (pH range 5.5 to 7.4) (Mitsch and Gosselink, 2000). While the pH of the compost materials will adjust when introduced to field conditions, the extent of that adjustment is unknown. Differences in the pH of the organic amendments and the “target” pH of the mitigation wetland soil will lead to differences in soil chemistry in terms of nutrient availability, nutrient release and sorption behavior.

The quantity and quality of organic matter differed between the compost samples and the natural wetland soil samples. The composts had significantly less organic matter, 25.9% and 28.5% for the lobster and leaf composts, respectively, as compared to the wetland soils (76.2% and 93.1% for the muck soil and the peat soil, respectively). Organic matter is a governing factor of several wetland soil characteristics such as, water holding capacity, plant nutrient supply, and pollution retention. As such, the comparatively lower organic matter content of the composts would presumably result in an incongruent functional capacity as compared to the natural wetland soil samples.

Based on elemental, ATR-FTIR, and <sup>13</sup>C-NMR analyses, the four organic materials differ in chemical and structural composition. The wetland soils have a higher



polarity than the composts. The polarity of the wetland soils appears to be attributed to a higher polysaccharide content illustrated by the ATR-FTIR and  $^{13}\text{C}$ -NMR spectra. The polarity of the composts is ascribed to the presence of phenolic compounds such as tannins. These differences may be important when examining pollutant sorption potential.

All four organic materials are mainly comprised of aliphatic C ( $\geq 67\%$ ). High aliphatic content in soil organic matter has been ascribed to the presence of decay resistant plant cuticular materials such as: cutan and cutin (Zech et al, 1990; Köger-Knabner et al, 1997; Chefetz et al., 2002). The aliphaticity of soil organic matter has been linked to sorption of hydrophobic organic contaminants (HOC) (Chefetz et al., 2000; Kang and Xing, 2005). Recently, the polarity of soil organic matter has been suggested to have a more predominant role in HOC sorption (Kang and Xing, 2005). Compositional and structural differences between the compost samples and the wetland soils in this study illustrate the effect of source material on organic matter quality and subsequent functionality.

### **Nutrient Release Studies**

In general natural wetland systems tend to be nutrient poor in comparison to upland soils. Traditionally, wetlands are attributed with reducing nitrogen levels via denitrification (D'Angelo and Reddy, 1994) and phosphorus via sorption by sediments and organic matter (Woltemade, 2000). Recent studies have reported natural wetlands as possible phosphorus sources (Sallade and Sims, 1997b; Young and Ross, 2001). Likewise, studies have demonstrated initial nutrient release with the flooding of upland

agricultural soils (D'Angelo and Reddy, 1994; Pant et.al., 2002). Nutrient release studies performed for this research concluded that the selected composts had significantly higher levels of N and P release as compared to the wetland soil samples. In addition, the amount of P released by the composts under anaerobic conditions was two orders of magnitude higher than P release reported for natural wetlands, constructed wetlands, and flooded agricultural soils (Duxbury and Peverly, 1978; Moore et al., 1992; Corstanje and Reddy, 2004; Novak et al., 2004; Aldous et al., 2005; Dunne et al., 2005). A “first-flush” of nitrate was observed during the initial saturation of the compost samples indicating a potential for excessive levels of nitrate during the early establishment of mitigation wetlands, particularly in the absence of a vegetative cover. Overall, the results of the nutrient release portion of this research indicate that composts should be carefully examined in regards to being potential nonpoint pollutant (excessive nutrients) sources prior to their incorporation into mitigation wetland soils.

### **Nonpoint Source Pollution Retention Studies**

To assess the ability of the four organic materials to reduce nonpoint source pollutants, batch equilibrium sorption studies were performed using phosphorus and the commonly used herbicide, 2,4-D. For 3 of the 4 materials, phosphorus sorption was best fit to a single Langmuir isotherm. The phosphorus sorption maximum ( $S_{\max}$ ) of the four organic materials varied under aerobic and anaerobic conditions. The two wetland soils had higher  $S_{\max}$  values under aerobic conditions as compared to the leaf and lobster composts. Conversely, the lobster compost had the higher  $S_{\max}$  value under anaerobic conditions, which may be attributed to a high calcium content. In contrast to reported

studies on constructed wetlands (Dunne et al., 2005; Yoo et al., 2006), altered wetlands (Litaor et al., 2005), and natural wetlands (Reddy et al., 1998), oxalate-extractable aluminum and iron levels were not strongly related to either the aerobic or anaerobic  $S_{\max}$  of the four organic materials (Table 5.2). This lack of a correlation may be attributed to the overall low clay content of all for organic material as well as the clay mineralogy (younger, less weathered clays in the glaciated northeast as compared with oxide clays). A relationship between the level of oxalate-extractable phosphorus and phosphorus  $S_{\max}$  was observed. The oxalate-extractable phosphorus content may represent the total amount of phosphorus bound to amorphous metals (Fe, Al, and Mn). This suggests that although the content of the individual oxalate-extractable metals (Fe, Al, and Mn) did not correlate with phosphorus  $S_{\max}$ , the combination of phosphorus bound to oxalate-extractable Fe, Al, and Mn may be related to phosphorus  $S_{\max}$ . The  $EPC_0$  levels of the wetland soils were lower than the composts under both aerobic and anaerobic conditions. In addition, the  $EPC_0$  levels of the wetland soils were lower than the US EPA recommended phosphorus limit ( $0.1 \text{ mg P L}^{-1}$ ), indicating that the wetland soils would behave as phosphorus sinks as opposed to the compost samples, which would act as additional phosphorus sources.

The sorption of 2,4-D by the four organic materials was best described by the Freundlich isotherm. Notable differences were observed among the 2,4-D sorption parameters of the organic materials. More specifically, the wetland soils had greater  $K_{\text{om}}$  values than the compost samples. Results were consistent with previous studies, which report increased 2,4-D sorption with increased organic matter/carbon content and

decreasing pH (Weber, 1972; Spadotto and Hornsby, 2003; Dorado et al., 2003; Picton and Farenhorst, 2004). Overall, the selected composts exhibit a lower ability to reduce ecologically adverse concentrations of both phosphorus and 2,4-D.

### **Recommended Assay For Composts Utilized In Mitigation Wetlands**

Pearson's Correlations were performed to determine those chemical and physical characteristics that may adequately predict the performance of composts in mitigation wetlands (SAS Institute, Inc., 2004). Aerobic  $S_{\max}$  values were positively correlated with %OM and total carbon and negatively correlated with pH and oxalate extractable P (Table 5.2). Both aerobic P release and aerobic  $EPC_0$  values were positively correlated with oxalate-extractable P, Morgan's extractable P, and total P levels. In addition, aerobic  $EPC_0$  values were negatively correlated with %OM, total carbon and polarity.

Despite the comparatively higher 2,4-D sorption and organic matter content of the wetland soils as compared to the composts, a statistically significant correlation was not present (Table 6.1). Also, percent aliphatic carbon, percent aromatic carbon, and polarity were not significantly correlated with  $K_f$ . A significant negative correlation was, however, observed between  $K_f$  values and pH and total iron content.

Based on the results of this research, in particular the correlations between specific characteristics and phosphorus behavior (Table 5.2 and 6.2), the following chemical and physical analyses are recommended for the evaluation of organic amendments in mitigation wetlands: %OM, pH, Morgan's extractable P, and Total P. Oxalate-extractable P may also be measured as an indicator of potential P release and  $EPC_0$ . However, oxalate-extractable P is not commonly determined as compared to

Morgan's extractable P and total P, which are widely determined in soil/compost testing labs throughout the US.

Table 6.1. Pearson's correlation values of 2,4-D sorption  $K_f$  with selected soil parameters.

| Selected Parameter | 2,4-D Sorption |
|--------------------|----------------|
|                    | $K_f^a$        |
| pH                 | -0.9547*       |
| %OM                | 0.8420         |
| $C_{Total}$        | 0.8177         |
| Polarity           | 0.5685         |
| % aromatic C       | 0.8522         |
| % aliphatic C      | -0.8522        |
| $Fe_{Total}$       | -0.9676*       |
| $Mn_{Total}$       | -0.6925        |
| $Al_{Total}$       | -0.3317        |
| $Ca_{Total}$       | -0.7443        |

\* Significant at the 0.05 probability level

<sup>a</sup>  $K_f$ , Freundlich sorption coefficient

Table 6.2. Pearson's correlation values of  $PO_4^{3-}$  release attributes with selected soil parameters.

| Selected Parameter | $PO_4^{3-}$ Release |           |
|--------------------|---------------------|-----------|
|                    | Aerobic             | Anaerobic |
| pH                 | 0.7597              | 0.6644    |
| %OM                | -0.9396             | -0.7639   |
| $Fe_{Ox}$          | 0.0334              | -0.0386   |
| $Al_{Ox}$          | 0.3059              | 0.2405    |
| $Mn_{Ox}$          | -0.6400             | -0.8399   |
| $P_{Ox}$           | 0.9569*             | 0.7952    |
| $P_{Morgan}$       | 0.9980*             | 0.9396    |
| $P_{Total}$        | 0.9583*             | 0.07820   |
| $C_{Total}$        | -0.9452*            | -0.7644   |
| Polarity           | -0.9528*            | -0.9648*  |
| $EPC_0$            | 0.9994**            | 0.9069    |

\* Significant at the 0.05 probability level

\*\* Significant at the 0.01 probability level

The following thresholds have been determined based on plots of  $EPC_0$  vs. Morgan's extractable P and  $EPC_0$  vs. Total P. Under aerobic conditions, the  $EPC_0$  equals  $0.1 \text{ mg P L}^{-1}$  (U.S. EPA recommended limit) when the organic materials' Morgan's extractable P content equals  $111.8 \text{ mg kg}^{-1}$  and/or the total P content equals  $1482 \text{ mg kg}^{-1}$ . Under anaerobic conditions, the  $EPC_0$  equals  $0.1 \text{ mg P L}^{-1}$  (U.S. EPA recommended limit) when the organic materials' Morgan's extractable P content equals  $25 \text{ mg kg}^{-1}$  and/or the total P content equals  $1286 \text{ mg kg}^{-1}$ . Although the previous concentrations do not address the influence of mitigation wetland field conditions, they are presumably applicable to conditions during the initial creation of mitigation wetlands. As such, based on this research it is recommended that organic amendments used in mitigation wetlands have Morgan's extractable P content  $\leq 25 \text{ mg kg}^{-1}$  and/or the total P content  $\leq 1286 \text{ mg kg}^{-1}$ .

Based on the results of this study, pH has a governing role in the sorption of 2,4-D, with greater sorption occurring at highly acidic conditions. As the pH of natural wetlands varies depending on the type of system (with a majority of wetlands being circumneutral), an acidic environment is not always the goal from the perspective of replicating the characteristics of a lost or damaged natural wetland. Therefore, the utilization of highly acidic organic amendments is not recommended. However, a second factor governing 2,4-D sorption is the organic matter content of a soil/sediment (Table 6.1). Although a statistically significant correlation between 2, 4-D sorption and percent organic matter was not discovered in this study, a negative correlation between 2,4-D sorption and total iron was demonstrated. Comparatively low total iron content

suggests low mineral content and high organic matter content. As such, both the total iron and percent organic matter are recommended analyses for organic amendments in mitigation wetlands in respect to the ability to retain 2,4-D.

### **Suggested Future Work**

In light of the identified differences between selected commercial composts and organic wetland soils and the illustrated importance of source material on organic matter composition, further evaluation of mitigation wetland amendments is highly recommended. Further examination of organic materials from varying sources would be beneficial in the attempt to identify suitable organic amendments for mitigation wetlands. In addition to source material, the physio-chemical properties of composted materials may also vary with differences in composting practices just as natural soil organic matter may vary with age and decomposition. For example, the high nutrient content observed for the leaf compost evaluated in this study may differ from other commercially available leaf composts, or the same compost subjected to an increased decomposition period.

While the reduction of pollutants such as phosphorus and 2,4-D has been attributed to chemical sorption by soil and organic matter, biological processes occurring within the wetland environment may also affect pollutant concentrations. Microbial degradation of 2,4-D as well as phosphorus and nitrogen uptake studies by plants and microbes under aerobic and anaerobic conditions would provide a more thorough understanding of pollutant sinks within wetland environments.

It would be beneficial to perform field studies that compare the performance of natural reference wetland systems to mitigation wetland sites that use selected compost materials from this study and additional commercial amendments. These studies could incorporate factors such as: the chemistry of hydrological inputs, wet and dry cycles, microbial populations, landscape inputs, and seasonal climate changes, which were not incorporated in the current laboratory study. A comparison between laboratory and field results would be beneficial to establishing applicable organic amendment testing parameters.

In 1986, Edward Maltby asserted that "more than any other part of the wetland system, the organic horizon component must be the most difficult to re-create, and for practical purposes this may be regarded as impossible". Such a statement should be viewed as a challenge, not a concession. As our nation's water supply dwindles in both quantity and quality, the role of wetlands, both natural and created, as purifying systems becomes increasingly important. As such, the goal of truly understanding wetland organic matter and, with that understanding, successfully mitigating function as well as quantity, is as necessary as it is seemingly daunting.



**APPENDIX A**

**PHOSPHORUS SORPTION GRAPHS**

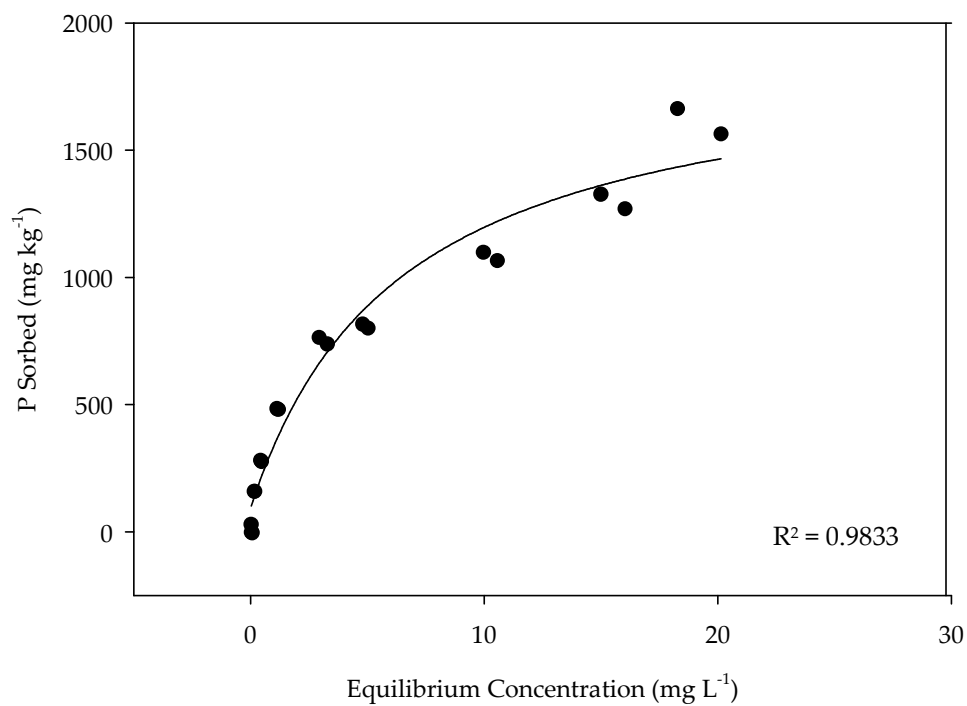


Figure A.1. Sorption of phosphorus by muck soil under aerobic conditions.

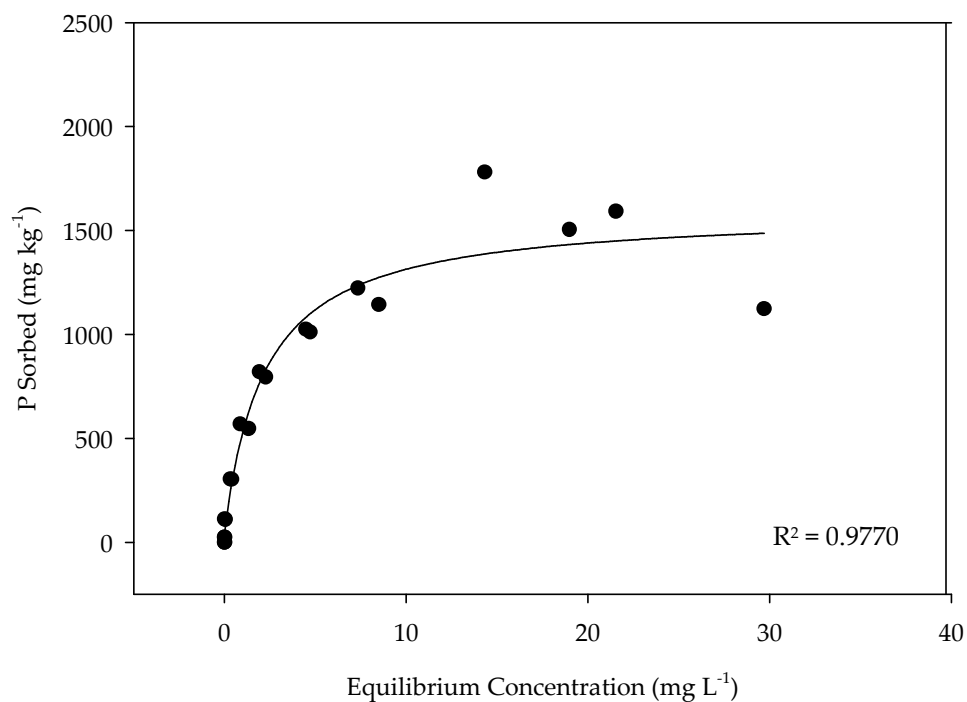


Figure A.2. Sorption of phosphorus by muck soil under anaerobic conditions.

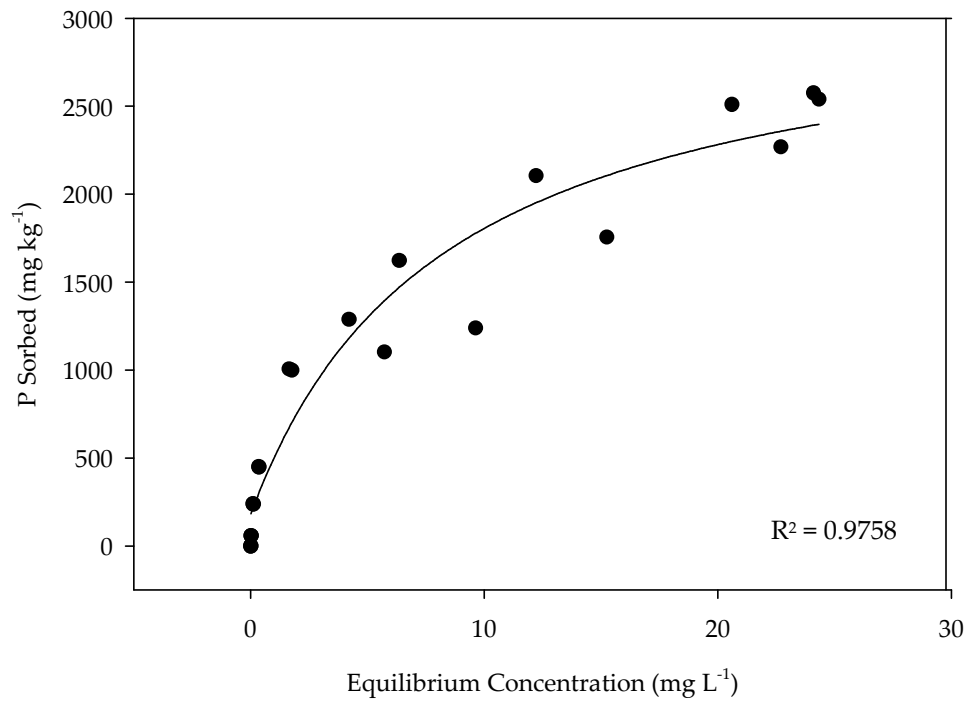


Figure A.3. Sorption of phosphorus by peat soil under aerobic conditions.

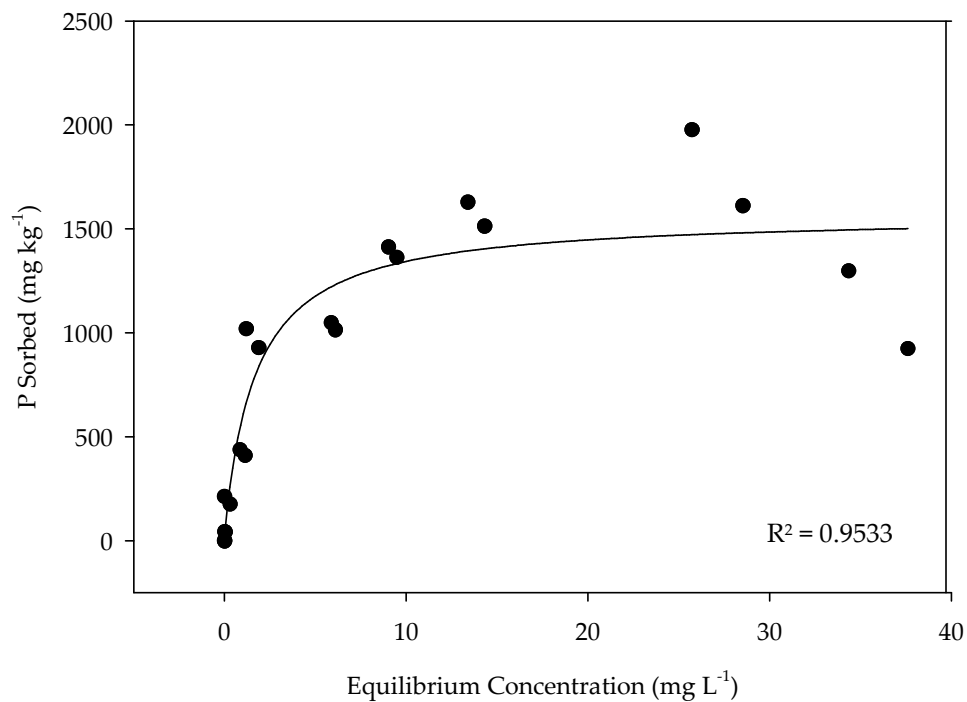


Figure A.4. Sorption of phosphorus by peat soil under anaerobic conditions.

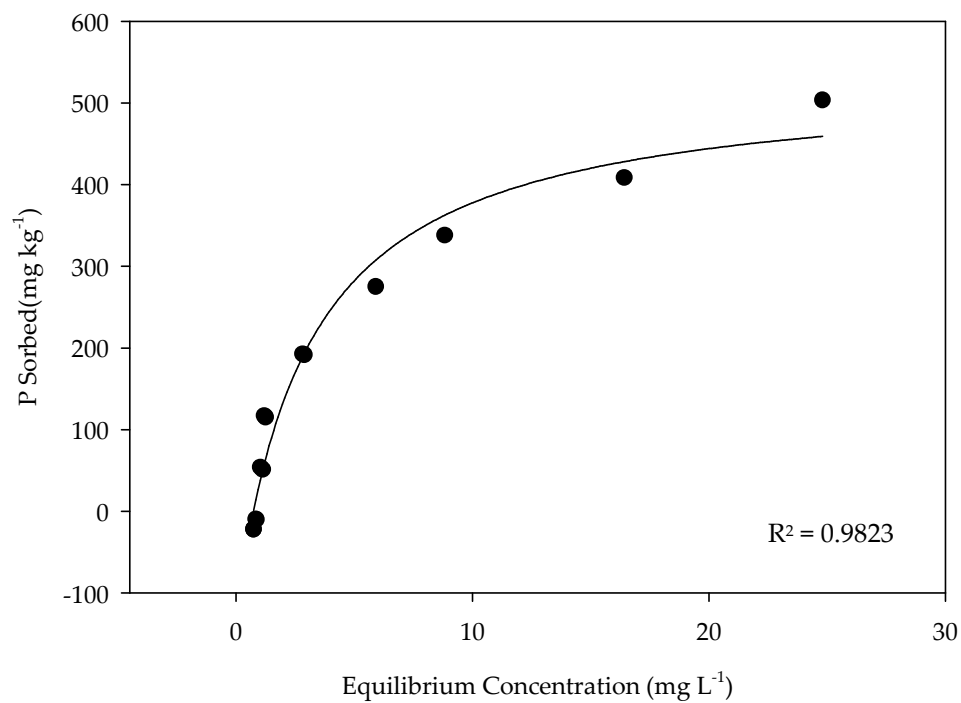


Figure A.5. Sorption of phosphorus by lobster compost under aerobic conditions.

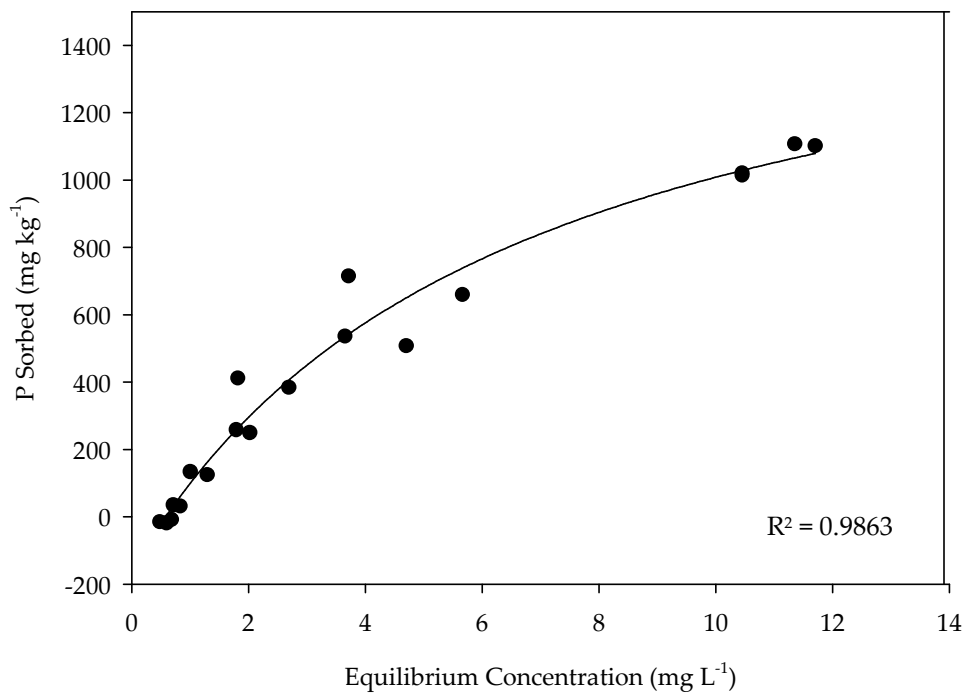


Figure A.6. Sorption of phosphorus by lobster compost under anaerobic conditions.

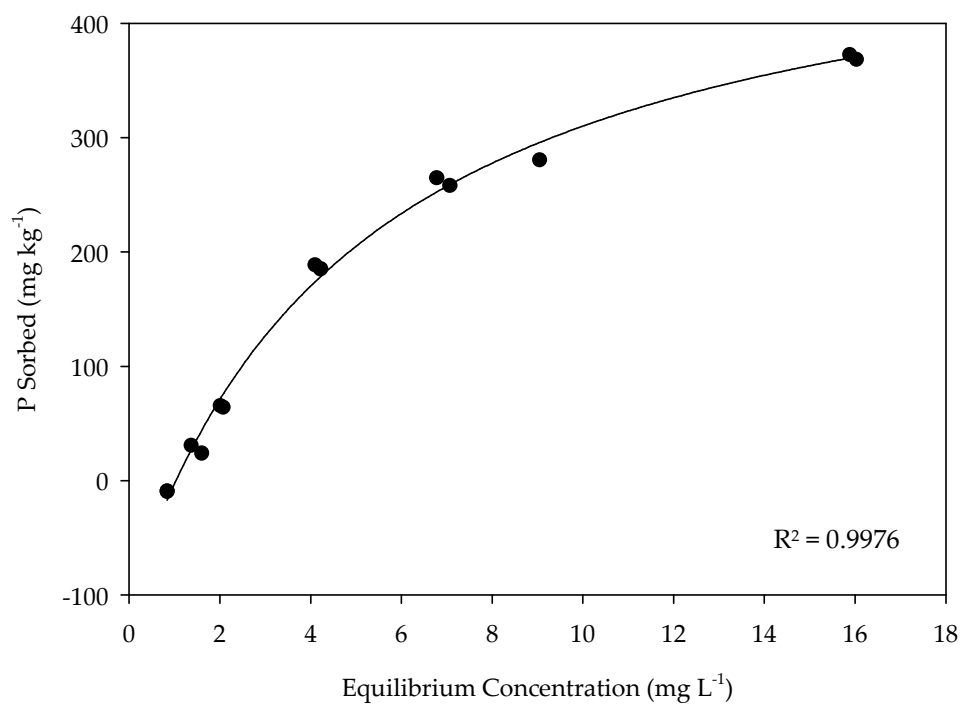


Figure A.7. Sorption of phosphorus by leaf compost under aerobic conditions.

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